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IODOPHORS AS SANITIZING AGENTS[1]

BY C. K. JOHNS

ABSTRACT

Representative iodophors have been compared against chlorine and quaternary ammonium germicides. Test organisms included *M. pyogenes* v. *aureus*, *E. coli*, and *P. aeruginosa*. Solutions with and without 0.5% added skim milk were tested by a modified Weber and Black method at 5°, 20°, and 45° C. The iodophors compared very favorably with a quick-acting hypochlorite, especially in the presence of skim milk. Other products tested were appreciably slower. In the "capacity" test the iodophors showed up extremely well, frequently destroying many more "increments" of test organism than other germicides at eight times greater concentration. Exceptionally favorable results with spores of *B. subtilis* were subsequently found to be due to the bacteriostatic effect of certain nonionic constituents of the iodophors.

While the germicidal value of elemental iodine has long been recognized, its high vapor tension, corrosiveness, toxicity and low solubility in aqueous solution have made it unsuitable for use as a sanitizing agent in the dairy and food industries. However, recent research (11) has resulted in the development of products containing iodine wherein these defects are largely overcome. In these new products, called "iodophors" (11), the iodine is loosely combined with suitable nonionic wetting agents which act as "carriers", while acid, generally phosphoric, is added to increase the germicidal activity and promote stability. Lazarus (10) has reported favorable results from a field test among farms in the Cleveland area, where an iodophor detergent sanitizer was substituted for the conventional sanitizing agent. In view of the advantages claimed for this new class of product, extensive studies were undertaken at Ottawa.

EXPERIMENTAL

Preliminary tests were conducted to determine (*a*) the corrosiveness of these iodophors for stainless steel and tinned iron, and (*b*) the effect on the flavor of milk.

Corrosion of stainless steel was negligible; that of tinned steel was no greater than that noted when using a liquid hypochlorite (Dalglish), and much less than with Antibac, an acid-type chlorine compound (2, 9), while

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Contribution No. 369 from the Bacteriology Division, Science Service, Department of Agriculture, Ottawa, Canada.

amounts as great as 10 p.p.m. of iodine failed to impart an off-flavor to milk either before or after pasteurization.

Materials and Methods

Preliminary tests with four iodophors revealed comparable germicidal effectiveness. Consequently, for the main studies two were chosen. These were Iosan, a detergent-sanitizer formulation recommended for use at 25 p.p.m. (1:640 dilution), and Iobac, a straight germicide recommended for use at from 7.5 p.p.m. (1:1280) (recirculation) to 15 p.p.m. (1:640) (fogging or spraying). Preliminary tests having shown that the effectiveness of these iodophors was only slightly diminished by hard water, distilled water dilutions were employed throughout.

To establish their relative effectiveness, the two iodophors were compared against the following products, distilled water solutions of which at 100 p.p.m. gave the pH values shown in parentheses:

Dalglish liquid hypochlorite (8.7)
Diversol—chlorinated phosphate (11.2)
Antibac—1,3-dichloro, 5,5-dimethyl hydantoin (5.0)
Roccal—alkyl dimethyl benzyl ammonium chloride (5.0)
Hyamine 2389—alkylated (C_9–C_{15}) tolyl methyl trimethyl ammonium chlorides (5.5)
Diokem—sodium hypochlorite plus sodium metasilicate, trisodium phosphate, etc. (11.4)

The test organisms used in the main tests were:
Micrococcus pyogenes v. *aureus*, BDR 490
Escherichia coli BDR 117
Pseudomonas aeruginosa BDR 499

After several daily transfers on Bacto penassay base agar, the 24 hr. growth was washed off with buffered distilled water (1) and diluted to give a plate count of approximately 200,000,000 per ml. Where tests were made to determine the effect of organic matter, 1% of sterile skim milk was added to the suspension.

In place of the glass slide method formerly employed here (7), a modification of the Weber and Black (13) method was used, as this method has been most generally used by recent investigators of sanitizing agents. Previous work here (5) had shown good agreement between the results of the Weber and Black and glass slide tests, although the latter reached the end point earlier. The chief modifications (6) introduced into the Weber and Black test were (*a*) pipetting of 1 ml. of medication mixture into 2 ml. of suitable inhibitor solution in a Petri dish set at a slight angle from the horizontal, (*b*) reducing the exposure periods to 7.5, 15, 30, and 60 sec., and (*c*) substitution of small wide-mouthed jars for test tubes to hold the medication mixture.

To supplement this method, a "capacity" test, based on that described by Cantor and Shelanski (3), was employed. One-hundred-milliliter portions of germicide in 300-ml. wide-mouthed flasks were inoculated with 1 ml. of a

bacterial suspension diluted 1: 1 with sterile skim milk; after 30 sec. 1 ml. was plated out. This procedure was repeated at five-minute intervals for 60 min.

Additional tests were conducted using spore suspensions of *Bacillus subtilis* (Bacto No. 453), wherein 1 ml. of suspension containing 1,000,000 spores per ml. was introduced into 100 ml. of germicide as in the "capacity" test, and portions plated directly at appropriate intervals.

RESULTS AND DISCUSSION

As each product was run on at least three concentrations, with four exposure periods, with and without added skim milk, at three temperatures, and sometimes replicated five to seven times, the data obtained are too extensive to be presented in their entirety. To facilitate comparison of the effects of these various factors on the several types of germicide, the destruction of 99.9999% of the test organisms was taken as the end point (12). The concentrations required to reach this end point within 30 sec. for each product are presented graphically in Figs. 1–3.

Dalglish, a liquid hypochlorite widely used in Canada, was used as a standard for comparison, it having previously been shown to possess a high degree of germicidal speed (7, 9). It will be seen that Dalglish, unlike most germicides, is practically unaffected by the temperature. (A similar lack of temperature effect had been previously noted (8) with a calcium hypochlorite, BK, while Dvorkovitz and Crocker (4) reported the same finding. This is in contrast to Weber and Levine's (14) finding that, for chlorine water, a drop of 10° C.

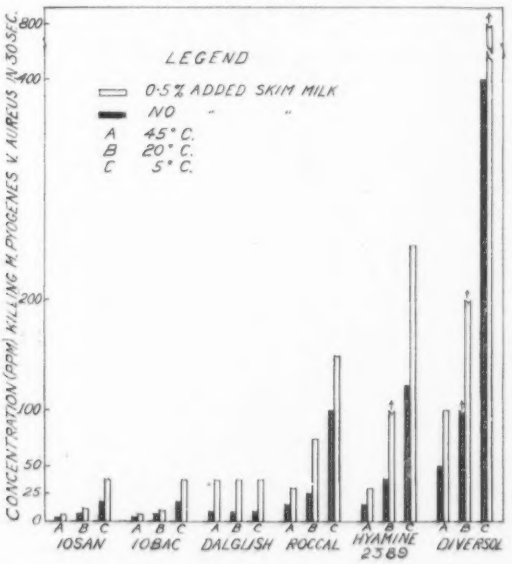

FIG. 1. Showing effect of temperature and organic matter (skim milk) on the germicidal efficiency of selected products against *M. pyogenes* v. *aureus*.

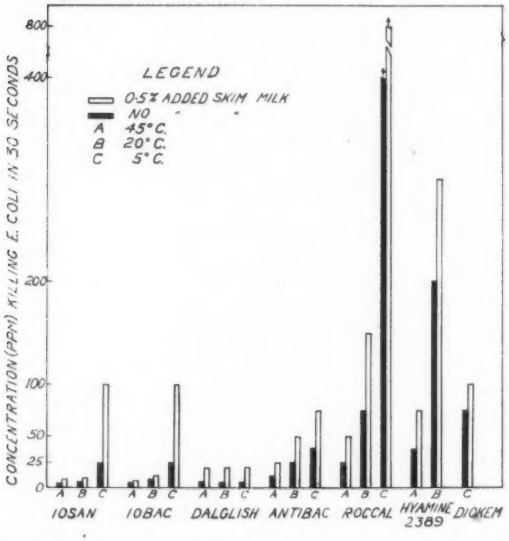

FIG. 2. Showing effect of temperature and organic matter (skim milk) on the germicidal efficiency of selected products against *E. coli*.

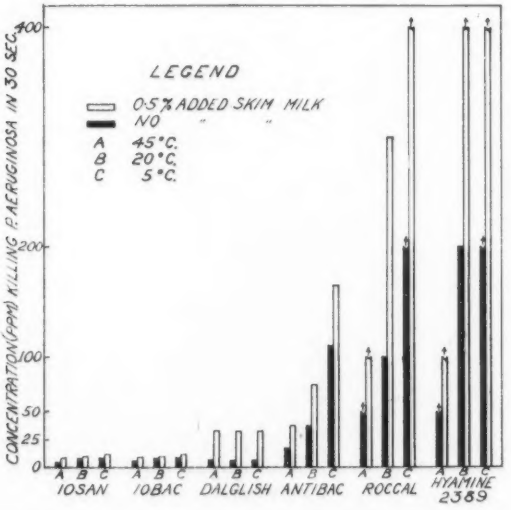

FIG. 3. Showing effect of temperature and organic matter (skim milk) on the germicidal efficiency of selected products against *P. aeruginosa*.

required a twofold increase in the exposure period.) It is, however, affected by the presence of 0.5% skim milk almost twice as much as any of the others.

Against *M. pyogenes* v. *aureus* (Fig. 1) the iodophors are superior to Dalglish with and without the presence of 0.5% skim milk at 45° and 20°, equivalent at 5° C. with skim milk and less effective in its absence. The quaternaries were decidedly slower, with Roccal the better of the two. Diversol, as in previous studies (7), failed to kill quickly enough, so was dropped from further tests.

Where *E. coli* was the test organism (Fig. 2), Dalglish was decidedly more effective than the iodophors at 5° C., and comparable at the higher temperatures in the absence of skim milk. The quaternaries were relatively less effective than against the Gram-positive organism. Antibac, substituted for Diversol, was again (9) less effective than Dalglish but superior to the quaternaries. Diokem, in a single test at 5° C., was surprisingly effective for so alkaline a product (pH 11.4 at 100 p.p.m.—compare with Diversol, Fig. 1).

The iodophors appear to best advantage against *P. aeruginosa*. Both temperature and organic matter had less effect here. Conversely, the other products all required appreciably higher concentrations than against *E. coli*.

The results obtained with the "capacity" test are summarized in Table I. The superiority of the iodophors is very evident, the more so since they were used at concentrations approximately one-eighth of those used with the other products. The single test with Diokem also revealed that this product possesses unusual capacity, even in the presence of considerable concentrations of milk. (After 12 increments had been added the medication mixture contained 6% of skim milk.)

As quaternary ammonium compounds are generally most effective against Gram-positive organisms, an additional capacity test was subsequently run

TABLE I

RESULTS WITH CAPACITY TEST

Solution at 20° C.; increments of bacterial suspension in 50% skim milk added at 5 min. intervals: figures represent number of increments destroyed (99.99% kill as end point)

Product	Conc. (p.p.m.)	Test organism		
		M. pyogenes v. *aureus*	*E. coli*	*P. aeruginosa*
Iosan	28	8	8	9
Iobac	28	6	8	10
Biopal CVL-10 + phosphoric acid	28	7	—	—
Biopal CVL-10 + hydroxyacetic acid	27	6	—	—
Dalglish	200	3	4	3
Antibac	200	—	9	7
Roccal	200	—	5	3
Hyamine 2389	200	—	3	—
Diokem	200	—	14*	12*
Diversol	200	—	5	—

* *Maximum number of increments tested.*

comparing Roccal (200 p.p.m.) with five other solutions. To our surprise, counts were reduced to near zero after 12 increments. A repeat test confirmed this, and gave a similar result with Hyamine 2389. For further information, Roccal was run at 25, 50, and 100 p.p.m., while in one set of tests a second plating of the medication mixture was conducted after five minutes exposure. The results from these and other supplementary studies are shown in Table II. From these data it is evident that the capacity of the quaternaries falls off appreciably at concentrations below 100 p.p.m. so that at 25 p.p.m. they are much less effective than the iodophors. These tests again bring out the marked differences in the behavior of the several test organisms to the various germicides being tested here.

TABLE II

SUPPLEMENTARY CAPACITY TEST STUDIES WITH *M. pyogenes* v. *aureus* AT 20° C.
END POINT = 99.99% KILL

Product	Concentration (p.p.m.)	Number of increments taken care of in	
		30 sec.	5 min.
Iosan	25	6–8 (4)	10 (1)
Iobac	25	4–6 (2)	—
Roccal	25	1 (1)	1 (1)
"	50	7 (1)	10 (1)
"	100	11 (1)	12* (1)
"	200	12* (2)	12* (1)
Hyamine 2389	200	12* (1)	—
Dalglish	200	3 (2)	3 (1)
Antibac	100	4 (1)	—
"	200	9 (1)	—
Diokem	100	0 (1)	—
"	200	0 (1)	3 (1)

N.B. Figures in brackets indicate number of tests made.
* *Maximum number of increments tested.*

Tests carried out with spores of *B. subtilis*, using the direct plating method, showed the iodophors to be far more effective at 25 p.p.m. than Dalglish at 200 p.p.m. Subsequent tests by Dr. H. Katznelson of this Division, using spores of *Bacillus larvae*, indicated that even though the iodine was all neutralized by thiosulphate in the direct plating method, the mixture was highly toxic for these spores. Comparison of results obtained by a dilution technique with those by direct plating, using *B. subtilis*, revealed that this held true here, but to a lesser degree. The inhibitory effect was traced to certain nonionic constituents; this could be neutralized at concentrations up to 25 p.p.m. by the incorporation of 2% skim milk in the plating medium in the direct plating method. Using the dilution technique, the iodophors, instead of being so much more effective than Dalglish, were decidedly less so, almost half of the

spores surviving 20 min. exposure to 200 p.p.m. iodophor solution at 20° C. Initial comparison of direct plating vs. dilution techniques with *M. pyogenes* v. *aureus* had given identical results. Subsequent comparisons showed that results with *P. aeruginosa* were slightly affected, and those with *E. coli* more seriously affected, necessitating the repetition of the tests with these organisms. Figs. 1–3 show the revised results.

In view of the possible decrease in acidity of an iodophor solution passing over equipment not freed from residual alkaline detergents, tests were made to determine the effect of pH on germicidal activity. It was found difficult to shift the pH from around 2.8, the usual range for 25 p.p.m. Iosan and Iobac. Finally, a double strength buffer solution at pH 5 was employed to dilute the iodophors. A single test with *M. pyogenes* v. *aureus* showed that the concentration required for equivalent killing at pH 5 was approximately double that at the usual pH level.

Among the several advantages of the iodophors may be listed the fact that the strength is indicated by the color, a pale tinge of yellow remaining at 5 p.p.m. There is thus little excuse for the continued use of an exhausted solution. Again, on account of their acidity iodophor solutions prevent the formation of milkstone or other film on dairy utensils and equipment, even with hard water. Furthermore, milkstone was actually removed from a milker inflation by repeated brief immersions in 25 p.p.m. Iosan solution. Limited practical trials on selected farms with Iosan at 25 p.p.m., and on milk handling and processing equipment with Iobac at 7.5 p.p.m., have given very satisfactory results. In view of their great germicidal activity and "capacity", and of the advantages mentioned above, iodophors appear very promising. They deserve extensive field trials to confirm the encouraging results obtained in the present studies.

ACKNOWLEDGMENTS

Grateful acknowledgment is made of the technical assistance of Miss Shirley Armstrong and Mr. J. G. Desmarais in carrying out the laboratory tests.

REFERENCES

1. American Public Health Association. Standard methods for the examination of dairy products. 9th ed. New York, N.Y. 1948.
2. Bacon, L. R. and Sotier, A. L. J. Milk and Food Technol. 15: 285–293. 1952.
3. Cantor, A. and Shelanski, H. A. Soap Sanit. Chemicals, 27(2): 133–137. 1951.
4. Dvorkovitz, V. and Crocker, C. K. Soap Sanit. Chemicals, 26(9): 114–119. 1950.
5. Humphreys, T. W. and Johns, C. K. J. Milk and Food Technol. 16: 186–188. 1953.
6. Humphreys, T. W. and Johns, C. K. Appl. Microbiol. 2: 1. 1954.
7. Johns, C. K. Sci. Agr. 14: 585–607. 1934.
8. Johns, C. K. Unpublished results. 1950.
9. Johns, C. K. J. Milk and Food Technol. 14: 134–136. 1951.
10. Lazarus, N. E. Milk Dealer, 42(1): 45; 68–71. 1952.
11. Terry, D. H. and Shelanski, H. A. Modern Sanit. 4: 61–65. 1952.
12. Weber, G. R. Pub. Health Repts. (U.S.), 65: 503–512. 1950.
13. Weber, G. R. and Black, L. A. Am. J. Public Health, 38: 1405–1417. 1948.
14. Weber, G. R. and Levine, M. Am. J. Public Health, 34: 719–728. 1944.

ESTIMATION OF PROTEIN DENATURATION IN FROZEN MILK[1]

By Dyson Rose[2]

ABSTRACT

The volume of milk solids settled by a standard centrifugation procedure gives a rapid and convenient measure of denaturation during frozen storage, but to obtain acceptable results, close control of temperatures and holding times during preparation of samples for centrifugation is necessary. Density of the precipitate, and therefore its volume, is also affected by the force and duration of centrifugation, pH, and other undetermined factors. For studies requiring more accurate data, a determination of total nitrogen in the supernatant milk is recommended.

INTRODUCTION

During storage of frozen milk a gradual denaturation of milk protein occurs (5, 8), and denatured protein precipitates when the milk is centrifuged. The volume of milk solids settled by a standard centrifugation is usually accepted as a measure of this change (1, 2, 3, 4, 7). This "volume of precipitate" test is sensitive to changes in the stability of milk colloids, but variations in density and redispersibility of the precipitate make it only semiquantitative. It, therefore, seemed desirable to compare the volume of precipitate with a more absolute measure of the amount of protein precipitated before undertaking an investigation of the physical and chemical changes occurring during frozen storage of milk.

Determination of casein in a precipitate that had been freed from unprecipitated milk solids would be the most absolute measure of protein precipitation (5, 9), but no method of washing the precipitate is available. Correction of the analyses of unwashed precipitates for soluble solids of the fluid phase is difficult and inaccurate. Analysis of the supernatant milk thus appeared to be the most accurate procedure available. The relative effect of various factors on volume of precipitate and on loss of nitrogen from the supernatant was therefore studied.

MATERIALS AND METHODS

Pasteurized whole milk from a local dairy was used as received, or concentrated in a Mojonnier "Lo-Temp" evaporator at a milk temperature of 20–21°C. (69–70°F.). Hundred milliliter samples of milk or concentrate were frozen and stored at −12°C. (+10°F.) in sealed 2-11/16 × 4-00/16 in. cans. Samples were thawed by placing unopened cans at 4°C. (40°F.). Except where otherwise stated, concentrated milks were rewatered with distilled water at room temperature.

Volume of precipitate was estimated by centrifuging 50 ml. of each sample for 10 min., at 725 R.C.F. at tip, in graduated conical tubes, except when

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[2] *With the technical assistance of H. Tessier and J. Marier.*

centrifugation time and force were being investigated. Total nitrogen and noncasein nitrogen were determined by Rowland's procedures (6) adapted to micro-Kjeldahl determinations. Total solids were determined by mixing with sand and drying for 18 hr. at 105°C.

EXPERIMENTAL AND RESULTS

Sampling of Supernatants

Precipitation of casein reduces the total nitrogen content of the supernatant milk, but because stratification may occur during centrifuging, analysis of an aliquot of the supernatant will give satisfactory results only when the whole volume is collected and thoroughly mixed before withdrawal of the aliquot. Three methods of collecting the supernatant milk from partially precipitated samples were therefore compared: direct decantation, gentle suction through a hypodermic needle with the tip sealed and an opening made on the side about 1/16 in. from the tip, and immersion of the centrifuge tube to the observed precipitate level in a dry ice – alcohol bath for two minutes followed by decantation. The supernatant milk was analyzed for total solids, total nitrogen, and noncasein nitrogen.

With skim milk, the three methods of decantation gave essentially the same results, indicating that stratification of milk solids within the supernatant fluid did not introduce serious errors. With whole milk, the fat layer failed to decant uniformly and the data were therefore less reproducible. Less fat was included in the supernatants removed by suction, but even with this method the data were more variable than those obtained with skim milk. In spite of this slight superiority of the suction method when applied to whole milk, direct decantation of the supernatant appeared to be the most satisfactory procedure for routine use.

Effect of Thawing and Rewatering Conditions

Since precipitate formed during short periods of storage is readily redispersed by heat (4), thawing and rewatering techniques require standardization. Thawing by the addition of hot water will redisperse more precipitate than thawing at a controlled temperature close to the freezing point. However, even at low thawing temperatures gradual dispersion of the precipitate may occur. The effect of duration of holding at 4°C. was therefore investigated.

Samples of frozen concentrate were thawed by storing overnight at 4°C., rewatered, and combined to give a uniform initial dispersion, then held an additional 6, 24, or 48 hr. at 4°C. before being analyzed. A significant decrease in volume of precipitate and increase in total nitrogen in the decantate with increasing holding time was observed (Table I). When triplicate individual cans were analyzed after 6, 18, and 30 hr. at 4°C., the differences between the averages were not significant because of the large variability between cans. However, the average volume of precipitate for triplicate cans decreased from 11.64 to 10.34% during this holding period, suggesting that a slow redispersion of the precipitate may have occurred at 4°C. even in the concentrated milk.

TABLE I

REDISPERSION OF MILK SOLIDS AT 4°C. AFTER STORAGE AT −12°C.
(Averages of duplicate centrifugations on each of two lots of bulked milk samples)

Holding time, hr.	Vol. of ppt., % v/v	Total N in supernatant, mgm./ml.
0	13.4 ± 0.37	3.56 ± 0.07
6	13.3 ± 0.37	3.78 ± 0.07
24	12.1 ± 0.37	4.02 ± 0.07
48	11.1 ± 0.37	4.30 ± 0.07

Rewatering concentrates at 4°C. with water at 32°C. did not raise the milk temperature sufficiently to change the volume of precipitate, provided the sample was centrifuged at once, but, when samples were held for 20 min. at room temperature, the volume of precipitate increased significantly (+0.86% v/v). However no decrease in total nitrogen in the decantate was observed, indicating that the change in precipitate volume was caused by swelling of the precipitate and not by additional denaturation of casein.

The effect of short periods at moderate temperatures on volume of precipitate and nitrogen in the decantate was investigated further. Samples of concentrated skim milk, which had been stored for four and for six weeks at −12°C., were heated to 10°, 21°, and 32°C. for 10 min., then cooled to approximately 4°C. and centrifuged. Samples were heated before or after rewatering, and with and without stirring.

The volume of precipitate in samples stored either four or six weeks (Table II) decreased significantly with each temperature increment, but the difference between 10° and 21°C. was considerably less than that between 21° and 32°C. Stirring also reduced the volume of precipitate in samples stored six weeks, but had no significant effect on four-week samples. Heating to 10° and 21°C.

TABLE II

EFFECT OF MILD HEAT AND AGITATION ON VOLUME OF PRECIPITATE
(Averages of duplicate centrifugations)

Treatment		Volume of precipitate, % v/v					
Type of milk heated	Stirring	Sample *1, heated to			Sample *2, heated to		
		10°C.	21°C.	32°C.	10°C.	21°C.	32°C.
Concentrated	No	9.0	8.8	7.6	17.5	17.4	15.5
Rewatered	No	8.5	8.7	5.5	17.8	16.7	14.7
Concentrated	Yes	8.6	8.6	7.7	14.9	14.1	14.5
Rewatered	Yes	8.8	8.0	5.2	16.2	15.7	10.8
Average		8.72	8.52	6.50	16.60	15.98	13.88

Standard deviations—of average values for duplicate centrifugations ±0.6.
—of temperature averages ±0.29.
**Samples 1 and 2 had been stored at −12°C. for four and six weeks respectively.*

had the same effect on the concentrate as on the rewatered milk, but heating to 32°C. reduced the volume of precipitate in the rewatered milk more than in the concentrates.

Total nitrogen in the decantate (Table III) increased with increasing temperature, and at 32°C. was higher in milk rewatered before heating than in that rewatered after heating, inversely correlating with the volume of precipitate. However, agitation had no significant effect on total nitrogen values, suggesting that stirring the six-week samples did not redisperse the precipitate, but merely caused it to pack more densely during centrifugation.

TABLE III

EFFECT OF MILD HEAT AND AGITATION ON NITROGEN CONTENT OF THE DECANTATE
(Averages of duplicate centrifugations)

Treatment		Total nitrogen in decantate, mgm./ml.					
Type of milk heated	Stirring	Sample *1, heated to			Sample *2, heated to		
		10°C.	21°C.	32°C.	10°C.	21°C.	32°C.
Concentrated	No	5.07	4.99	5.48	3.13	3.32	3.51
Rewatered	No	5.04	5.30	5.66	3.24	3.34	4.13
Concentrated	Yes	5.10	5.27	5.39	3.48	3.46	3.93
Rewatered	Yes	5.21	5.20	5.83	3.36	3.45	3.77
Average		5.11	5.19	5.59	3.30	3.39	3.84

Standard deviation—of average values for duplicate centrifugations ±0.13.
—of temperature averages ±0.06.
**Samples 1 and 2 had been stored at −12°C. for four and six weeks, respectively.*

These data indicate that careful control of thawing and precentrifuging times and temperatures was required for reproducible results.

Effect of Centrifuging Conditions

Duplicate samples of a rewatered concentrate, prepared from whole milk and stored at −12°C. until about 12% precipitate developed, were centrifuged at 225, 500, and 900 R.C.F. at tip for 5, 10, and 15 min. The volume of precipitate decreased with increasing centrifugal force but the differences were not statistically significant. The volume of precipitate also decreased with increasing time (11.86, 10.36, and 10.26% v/v after 5, 10, 15 min., respectively, when averaged over all R.C.F. levels) and the difference between 5 and 10 min. was significant. Since no differences were detected in the total nitrogen of the supernatants, these changes in precipitate volume apparently were caused by packing.

Effect of Other Factors

Since the precipitate is largely casein (5, 9), precipitation causes a loss of nitrogen from the supernatant. The relation between volume of precipitate and loss of nitrogen is, therefore, an indication of precipitate density. Within

any one experiment there was a fairly close correlation between these two values, but samples subjected to a wide range of experimental conditions could vary markedly in volume of precipitate without a corresponding variation in total nitrogen. For example, varying the pH of a sample affected precipitate density. In samples adjusted to various acidities, concentrated 3 : 1, and stored at −12°C. (Fig. 1) precipitation of 1.5 mgm./ml. of casein nitrogen corresponded to precipitate volumes varying from 4% at pH 6.0 to about 16% at pH 7.1.

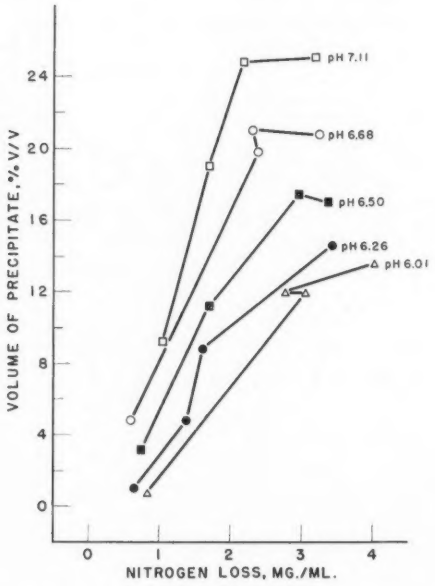

FIG. 1. Effect of pH on the volume of precipitate and loss of nitrogen from the decantate of 3 : 1 milk concentrate stored at −12°C. for 10, 17, 24, and 37 days. Connecting lines indicate chronological sequence of plotted points.

Various undetermined factors also affected the relation between nitrogen loss and volume of precipitate. To estimate the effect of these factors, 99 cans of skim milk were uniformly prepared and frozen in an 11 × 9 block at −12°C. Batches of six randomly selected cans were tested after four and five weeks (no precipitate developed earlier), and batches of 12 cans after each subsequent week. Duplicate aliquots from each can were centrifuged at about 30 min. intervals. Neither the standard deviation nor the coefficient of variation was statistically stable over all batches. Volume of precipitate and nitrogen measurements varied between duplicates to approximately the same extent, and the standard deviation of each averaged about 10% of the amount measured (Columns 3 and 6, Table IV). However, when different cans were compared, the variability of the "volume of precipitate" data increased to about

30% of the amount measured (Column 4, Table IV) while the variability of the nitrogen data only increased to approximately 15% of the amount measured (Column 7, Table IV). Much of the variability between cans was thus an uncontrolled variability in precipitate density rather than in the degree of protein denaturation, and the determination of total nitrogen was the more accurate of the two methods.

TABLE IV

VARIABILITY OF DATA FROM REPLICATE CANS AND DUPLICATE CENTRIFUGATIONS OF FROZEN SKIM MILK STORED AT −12°C.

(6 cans sampled at 4 and 5 weeks, 12 cans at 6 to 10 weeks)

Storage time, weeks	Mean vol. of ppt., % v/v	Coefficient of variation		Mean loss of nitrogen, mgm./ml.	Coefficient of variation	
		Between duplicate centrifugations	Between cans		Between duplicate centrifugations	Between cans
4	0.7	9	33	0.30	18	0
5	1.9	17	32	0.43	8	13
6	3.1	6	27	0.43	13	14
7	5.7	6	36	0.78	9	17
8	10.7	9	39	1.19	7	19
9	11.9	16	24	1.33	7	18
10	17.0	8	12	2.00	5	12

CONCLUSIONS

The "volume of precipitate" test for destabilized solids in frozen milk is rapid and convenient, and under standardized conditions can give a satisfactory indication of the extent to which milk has deteriorated. However, in studies designed to provide more exact information, volume of precipitate tests should be supplemented by estimation of total nitrogen in the supernatant milk. On the basis of data obtained in these studies the following recommendations are made:

1. Unless whole milk is of particular interest, skim milk should be used.
2. Samples should be thawed at or below 4°C. for a fixed time.
3. Samples should be kept below 21°C. during all preparatory and centrifuging steps, and the time involved should be kept constant.
4. Samples should be centrifuged for at least 10 min. at over 500 R.C.F. at tip.
5. The supernatant milk should be decanted, mixed, and analyzed for total nitrogen, and both nitrogen loss and volume of precipitate data recorded.
6. All tests should be adequately replicated.

ACKNOWLEDGMENT

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REFERENCES

1. BABCOCK, C. J. and STROBEL, D. R. J. Dairy Sci. 35: 195–198. 1952.
2. BELL, R. W. and MUCHA, T. J. J. Dairy Sci. 34: 432–437. 1951.
3. BELL, R. W. and MUCHA, T. J. J. Dairy Sci. 35: 1–5. 1952.
4. CORLEY, R. T. and DOAN, F. J. Food Research, 5: 369–378. 1940.
5. DOAN, F. J. and WARREN, F. G. J. Dairy Sci. 30: 837–848. 1947.
6. ROWLAND, S. J. J. Dairy Research, 9: 42–46. 1938.
7. TRACY, P. H., HETRICK, J., and KRIENKE, W. S. J. Dairy Sci. 33: 832–841. 1950.
8. WEBB, B. H. and HALL, S. A. J. Dairy Sci. 18: 275–286. 1935.
9. WILDASIN, H. L. and DOAN, F. J. J. Dairy Sci. 34: 438–445. 1951.

EFFECT OF FREEZING RATE ON STABILITY OF FROZEN MILK[1]

By Dyson Rose and H. Tessier

ABSTRACT

Milk and concentrated milk stored at −12°C. (+10°F.) (a temperature selected as the upper limit of normal commercial storage and handling conditions) were more stable when frozen slowly over several hours than when frozen in less than one hour. The least stable milk was obtained by freezing at a very rapid rate in liquid nitrogen. Storage life at −12°C. was also increased by holding partially frozen samples at −3°C. for up to 48 hr. before storage. Storage life at −18°C., the lower limit of readily available commercial storage facilities, was not greatly affected by freezing rate.

It is suggested that slow freezing allows time for the establishment of new equilibria under the stress of temperature and concentration changes, thus increasing the stability of the colloidal suspension.

INTRODUCTION

The storage of frozen milk or milk concentrate is severely limited by the precipitation of milk colloids. Precipitation of milk solids is markedly decreased as the storage temperature is lowered (1, 2, 3), but storage facilities below −18°C. (0°F.) are not readily available, and recent studies (8) indicate that temperatures above −18°C. are frequently encountered over a significant portion of the "turnover" period. Further studies on the stability of milk stored at temperatures between −12°C. (+10°F.), which can be accepted as the usual upper limit of normal storage temperatures, and −18°C. are therefore required.

The temperature at which a food product is frozen often influences its quality. Babcock *et al.* (1) reported that freezing milk at −40°C. for storage at −10°C. was detrimental, but their data do not permit direct comparison of samples of one lot of milk frozen at −40° and −10°C. and stored at −10°C. Other data on the effect of freezing rate or temperature are limited (6), and no attempt appears to have been made to study the effect of freezing rate (rate of ice formation) separately from the effect of per cent water frozen (freezing temperature). Such studies were therefore undertaken, and the results are presented in this paper.

MATERIALS AND METHODS

Tests were conducted over a period of several months on random samples of "pasteurized" or "homogenized" milk from a local dairy. Whole milk samples were canned within six hours of pasteurization, without further processing. Three-to-one concentrate was prepared in a Mojonnier "Lo-temp" evaporator at a milk temperature of 20° to 21°C. (68°–70°F.). The time for evaporation varied from one to three hours, depending on the amount prepared. Samples were then canned and placed in a freezer within two hours after concentration.

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Single-can samples were withdrawn from storage periodically, and analyzed for volume of precipitate and soluble nitrogen as previously outlined (9). Storage life was assessed from the volume of precipitate and from loss of casein nitrogen. Arbitrary limits of acceptability were set at 4% precipitate (v/v), or loss of 1 mgm. of casein nitrogen per milliliter of milk.

Samples having a short storage life were suitable for these tests, and no attempt was made to produce milk or concentrate of maximum keeping quality. Treatments, such as heating of the concentrate (4, 7), which appear to extend the over-all storage life without altering the relative effect of other factors, were therefore avoided.

EXPERIMENTAL AND RESULTS

Effect of Freezing Temperature

One hundred milliliter aliquots of pasteurized whole milk, and of concentrate, in sealed 2-11/16 × 4-00/16 in. cans were frozen in air at −7, −12, −23, and −40°C. (+20, +10, −10, and −40°F.) and by immersion in liquid nitrogen (−196°C.). Samples frozen in air were held at the temperature used for freezing for 24 hr. before storing at −12°C., those frozen by immersion in liquid nitrogen were placed at −40°C. overnight, then stored at −12°C.

The data for whole milk (Fig. 1) and concentrate (Fig. 2) indicate that

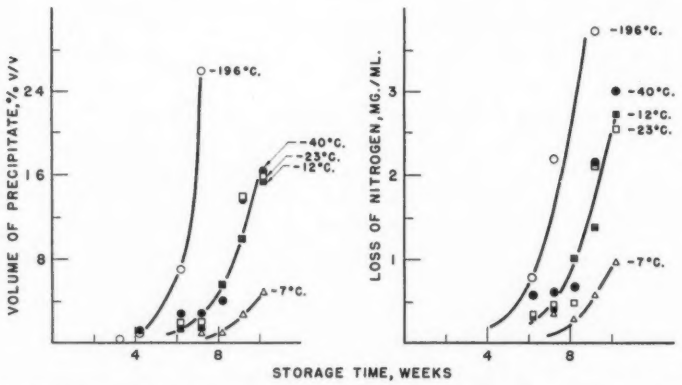

FIG. 1. Volume of precipitate and loss of nitrogen from whole milk frozen at various temperatures and stored at −12°C.

samples frozen at the extremely low temperature (−196°C.) had a very short storage life. Samples frozen at −40°, −23°, and −12°C. had a longer storage life, but no significant differences were encountered within this range of freezing temperatures. Samples frozen at −7°C. had the longest storage life. These observations were confirmed by a duplicate experiment with a second sample of milk.

To determine whether the freezing rate affected the stability of milk stored at various temperatures, cans of homogenized milk and concentrate were frozen at −7°, −12°, and −18°C. and samples from each freezing temperature

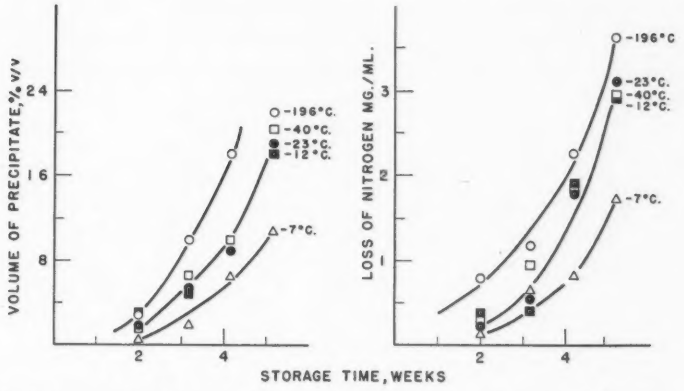

FIG. 2. Volume of precipitate and loss of nitrogen from 3 : 1 concentrate frozen at various temperatures and stored at −12°C.

were stored at −7°, −12°, and −18°C. As expected, storage life of the samples was greatest at −18°C. and least at −7°C. regardless of freezing temperature. With homogenized milk (Fig. 3) held at −7° and −12°C. the storage life of samples frozen at the higher temperatures was considerably greater than that of samples frozen at −18°C. With samples stored at −18°C. the effect of freezing temperature was slight. With concentrated samples the data (not reported) were more variable and, since all samples deteriorated rapidly, treatment differences were small. However the general trends confirmed the results for whole milk.

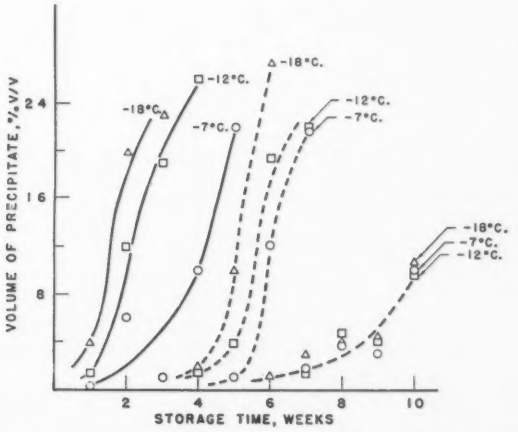

FIG. 3. Volume of precipitate from milk frozen at −7°, −12°, and −18°C. and stored at each of these temperatures.

Solid lines	—stored −7°C.	Circles	—frozen −7°C.
Short dashes	—stored −12°C.	Squares	—frozen −12°C.
Long dashes	—stored −18°C.	Triangles	—frozen −18°C.

Effect of Freezing Rate

Various freezing rates at a fixed final temperature were obtained by varying the rate of heat transfer, and are reported as the time required for the temperature at the center of a sample to drop from +10° to −7°C. (50° to 20°F.). Freezing time was determined in dummy cans in which a thermocouple was carefully centered in the milk. At −12°C., the freezing time for 100 ml. samples of pasteurized whole milk in 2-2/16 × 2-14/16 in. cans immersed in brine was $1\frac{1}{3}$ hr.; exposed in air, $5\frac{1}{4}$ hr.; insulated and frozen in air, 9 hr.

Data on "volume of precipitate" (Fig. 4) and on loss of casein nitrogen (not reported) indicate that the slow rate of freezing gave a more stable product.

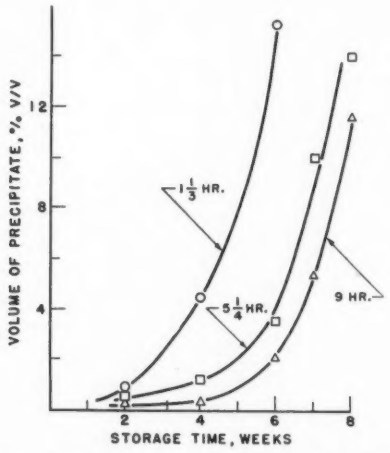

FIG. 4. Average volume of precipitate from two lots of whole milk frozen at various rates and stored at −12°C. Numbers beside the curves indicate the time required to freeze 100 ml.

The time required to develop 4% precipitate in samples frozen in $1\frac{1}{3}$ hr. was about 27 days, whereas in samples frozen in a 9 hr. period it was about 46 days. Increasing the freezing time thus increased the storage life by over 50% on the average of two tests.

In a further test, extremely slow freezing was obtained by initiating ice formation at −12°C., then transferring the cans to −3°C. for 24 or 48 hr. before completing the freezing at −12°C. The results obtained with concentrate stored at −12°C. (Table I) show that a marked improvement in keeping quality resulted from holding samples at −3°C. Holding at this temperature for 24 hr. appeared to be as effective as holding for 48 hr., and both treatments more than doubled the storage life.

Since the data of Fig. 3 suggested that freezing rate had only a slight effect when the milk was stored at −18°C., a further test was made in which insulated and exposed cans were frozen to a final temperature of −18°C. and stored at −18°C. At each sampling (Table II) samples frozen rapidly had a slightly

lower volume of precipitate than those frozen slowly. However, the slow-frozen samples were not consistently higher in soluble nitrogen, and it was concluded that freezing rate had no significant effect on storage life at this temperature.

TABLE I

EFFECT OF HOLDING PARTIALLY FROZEN MILK AT −3°C. ON ITS STABILITY DURING STORAGE AT −12°C.
(Single samples of 3 : 1 concentrate)

Storage time, weeks	Volume of precipitate, % v/v			Loss of casein-N, mgm./ml.		
	Control*	24 hr. at −3°C.	48 hr. at −3°C.	Control*	24 hr. at −3°C.	48 hr. at −3°C.
2	2.4	0.4	0.2	0.30	—	—
4	13.0	0.4	0.4	1.46	0.20	0.13
6	16.0	0.6	0.4	2.98	0.15	0.17
8	18.0	1.4	2.0	3.71	0.61	0.67
10	19.0	4.0	20.0	—	1.17	3.52

**Frozen at −12°C. without a holding period at −3°C.*

TABLE II

EFFECT OF FREEZING RATE ON THE STABILITY OF MILK STORED AT −18°C.
(Average of triplicate samples of whole milk)

Storage time, weeks	Volume of precipitate, % v/v			Loss of casein-N, mgm./ml.		
	Frozen in ¾ hr.	Frozen in 3-½ hr.	Frozen in 35 hr.	Frozen in ¾ hr.	Frozen in 3-½ hr.	Frozen in 35 hr.*
10	1.2	2.0	1.2	—	—	—
12	2.6	3.2	3.6	0.33	0.52	0.49
15	6.0	7.6	6.8	0.94	0.70	0.84
18	9.6	10.8	11.2	1.64	1.99	1.73

**Cans were insulated by a Dewar flask containing alcohol at −2°C., and the flask was exposed to air at −18°C. To avoid a prolonged supercooled period, ice formation was initiated by immersing the cans for two minutes in brine at −18°C. before placing them in the flask.*

Other experiments have shown that thawing and refreezing samples within 24 hr. of the initial freezing improved the stability during subsequent storage at −12°C. The effect of this treatment is presumably similar to that of slow freezing, but a single thawing–refreezing treatment had an adverse effect when carried out more than 24 hr. after the initial freezing.

DISCUSSION

Under the conditions used in these studies, very slow freezing produced a more stable product for storage at −12°C. than did freezing at the rate commonly used (1, 2). Extremely fast freezing in liquid nitrogen produced the least

stable product. Slow freezing was advantageous regardless of the method used to obtain it, and, on the average, storage life of slow-frozen samples was approximately 1.5 times that of the control samples when the storage temperature was −12°C. Holding partially frozen milk at the freezing point for 24 or 48 hr. before placing it at −12°C. doubled its storage life at −12°C. On the other hand, rate of freezing had little or no effect on the stability of samples stored at −18°C.

During freezing of milk, the concentration of milk solids is increased by the removal of water to form ice crystals. Precipitation of the less soluble salts probably occurs, and the chemical equilibria among the components are altered. Since some of the reactions involved are probably slow, rapid freezing would permit less change than slow freezing or temporary storage just below the freezing point. From the data presented in this paper, it may be assumed that one or more of these slow reactions increases the stability of milk stored at −12°C. Small lactose crystals are detrimental (10), but if the larger lactose crystals which probably form during slow freezing are less harmful, it is possible that lactose is responsible for this phenomenon. On the other hand, calcium concentration also affects stability (5), and the gradually increasing concentration induced by slow freezing may permit precipitation of calcium phosphate, while fast freezing may retain more calcium in a soluble form. Since short storage periods at about +5°C. before freezing are harmful (5), the concentration effect of ice crystal formation must be a major cause of the increased stability. However, the advantage gained by slow freezing is lost when milk is stored at −18°C.

These results are of no practical significance for long-term storage of frozen milk, but will be of interest if the milk is marketed locally through frozen food channels. This method of marketing appears quite feasible if turnover periods are kept below eight weeks, even though the temperature in display cabinets, and possibly at other stages of the marketing chain, rises to +10°F. Under these conditions a milk that has been frozen slowly would have a considerably greater stability than fast-frozen milk.

ACKNOWLEDGMENTS

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REFERENCES

1. Babcock, C. J., Roerig, R. N., Stabile, J. N., Dunlap, W. A., and Randall, R. J. Dairy Sci. 29: 699–706. 1946.
2. Bell, R. W. J. Dairy Sci. 31: 951–960. 1948.
3. Bell, R. W. and Mucha, T. J. J. Dairy Sci. 35: 1–5. 1952.
4. Corley, R. T. and Doan, F. J. Food Research, 5: 369–378. 1940.
5. Doan, F. J. Food Technol. 6: 402–404. 1952.
6. Doan, F. J. and Leeder, J. G. Food Ind. 16: 76–78; 123. 1944.
7. Doan, F. J. and Warren, F. T. J. Dairy Sci. 30: 837–848. 1947.
8. Munter, A. M., Byrne, C. H., and Dykstra, K. G. Food Technol. 7: 356–359. 1953.
9. Rose, D. Can. J. Technol. 32: 78–84. 1954.
10. Wildasin, H. L. and Doan, F. J. J. Dairy Sci. 34: 438–445. 1951.

THERMODYNAMICS OF THE COMBUSTION OF SODIUM-BASE PULPING LIQUORS[1]

By Thomas W. Bauer[2] and Rodger M. Dorland[3]

ABSTRACT

Thermodynamics has been used to calculate equilibrium constants of some reactions involved in the combustion of sodium-base pulping liquors such as kraft black liquor. Phase diagrams have been drawn to show the amounts of substances expected in the gas and solid (or liquid) phases. The reasons for sulphur and sodium losses are pointed out and means are suggested for their reduction.

INTRODUCTION

A recent paper (9*a*) has given equilibrium constants of chemical reaction equilibria in the combustion of sodium-base pulping liquors. The equilibrium constants themselves are, however, not a sufficient description of such a complicated system in which many simultaneous reactions may take place. There is also some criticism of the thermodynamic data used in the calculations.

The logarithmic equilibrium diagram method of Sillen and Andersson (13) permits a more graphical description of the equilibrium relations, showing clearly which substances will be present in the equilibrium mixture and their proportions.

The complicated substances of sodium-base pulping liquors break down in the furnace almost instantaneously into simple compounds which reduce the problem of thermodynamic calculations to one for a few inorganic substances. These substances are:

Na_2SO_4, Na_2S, Na_2CO_3, Na_2O, and NaOH as solids or liquids depending on the temperature;

C (solid) when not enough oxygen is present for complete combustion;

O_2, CO, CO_2, H_2, H_2O, S_2, SO_2, SO_3, H_2S, Na, and Na_2 in the gas phase.

Other substances such as polysulphides, sulphites, thiosulphates, CS_2, and COS will not be present in the furnace in significant amounts, although they might conceivably be formed in secondary reactions during cooling of the reaction products. Nitrogen and the inert gases present in air will not enter into the reactions except to act as diluents for the gas phase. The amount of dilution will, of course, affect the equilibria and this has been taken into account in formulating the assumptions on the relative amounts of the reacting substances.

THERMODYNAMIC DATA

The heats and free energies of formation of the substances under consideration were taken from the compilation by the U.S. National Bureau of Standards (10) with the following exceptions: The free energy of formation of

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$S_2(g)$ was calculated from the entropy value given by Kelley (6). The free energy of formation of Na_2S was taken from the calculations of Landiya (7). This value deviates considerably from the value given by May (9*a*), but it is in excellent agreement with the value derived from Latimer's entropy estimation (8). The free energy of formation of NaOH was calculated from data of Kelley and Snyder (3) and the thermodynamic data for monatomic sodium vapor were taken from the paper by Benton and Inatomi (1).

For the free energy equations at high temperatures, the heat capacity equations compiled by Kelley (5) were integrated. The data for Na_2SO_4, Na_2S, and Na_2CO_3 were recalculated from the experimental data given by May in his thesis (9*b*), with due regard to the heat of fusion and transition values reported by other investigators (10, 5). In the case of Na_2CO_3, there were not enough data available to consider the three transitions at 629°, 759°, and 891°K. In order to avoid complications from this source, the following calculations have been carried out for temperatures not too close to these transitions. Least squares and the method of Shomate (12) were used to derive the free energy equations from the experimental points where the accuracy of the data was sufficient. The heat of fusion of Na_2S derived in this manner was in rather good agreement with the value derived by Kelley (4) from the phase data of Friedrich (2). Since May's Na_2S was rather impure, it is not surprising that the small heat of fusion was obscured completely by premelting.

TABLE I

CONSTANTS OF FREE ENERGY EQUATIONS

$$\Delta F = \Delta H_0 + aT\log T + b(T^2/1000) + c(1000/T) + IT$$

Temp., °K.	Substance	ΔH_0	a	b	c	I
298–1600	C (graphite)	− 1,972	− 9.44	+0.51	+105	+28.944
298–1600	O_2 (*g*)	− 2,313	− 16.49	0.50	20	48.484
298–1600	CO (*g*)	− 28,521	− 15.63	0.49	5.5	24.386
298–1600	CO_2 (*g*)	− 97,978	− 24.29	1.08	102	71.750
298–1600	H_2 (*g*)	− 1,939	− 15.01	0.39	− 6.0	43.829
298–1600	H_2O (*g*)	− 60,023	− 16.51	1.28	− 4.0	59.347
298–1600	S_2 (*g*)	+ 27,036	− 19.66	0.14	39.5	18.557
298–1600	SO_2 (*g*)	− 74,643	− 23.90	1.27	71	68.289
298–1600	SO_3 (*g*)	− 99,867	− 31.55	3.21	156	115.331
298–1600	H_2S (*g*)	− 7,072	− 16.16	1.84	0	37.788
298–1600	Na_2O (*s*)	−104,320	− 36.15	2.70	0	136.675
298–1127	Na_2CO_3 (*s*)	−281,396	− 66.11	7.08	284.1	266.461
1127–1600	Na_2CO_3 (*l*)	−282,168	−100.99	0	0	365.843
298–1193	Na_2S (*s*)	− 95,529	− 48.87	0	0	150.875
1193–1600	Na_2S (*l*)	−131,337	−120.31	0	0	400.684
298– 513	Na_2SO_4 (*s* II)	−329,939	+ 22.47	52.31	−403	55.618
513–1163	Na_2SO_4 (*s* I)	−340,274	− 76.12	6.59	0	317.965
1163–1600	Na_2SO_4 (*l*)	−347,911	−120.44	0	0	452.739
298– 595	NaOH (*s*)	−107,715	− 44.21	0	0	165.599
595–1600	NaOH (*l*)	−106,430	− 46.97	0	0	171.096
298–1600	Na_2 (*g*)	+ 31,278	− 20.59	0	4.0	29.347

The constants of the free energy equations of the substances involved in the reactions are listed in Table I. Equations of the type

$$\Delta F = \Delta H_0 + aT \log T + b(T^2/1000) + c(1000/T) + IT$$

were used.

The heats and free energies of formation of the substances involved in the combustion at selected values of temperature have been given in Table II.

TABLE II

HEATS AND FREE ENERGIES OF FORMATION AT SELECTED VALUES OF TEMPERATURE
(in calories)

Substance	$\Delta H°$ 298.16°K.	$\Delta F°$ 298.16°K.	$\Delta F°$ 800°K.	$\Delta F°$ 1000°K.	$\Delta F°$ 1200°K.	$\Delta F°$ 1400°K.	$\Delta F°$ 1600°K.
C (graphite)	0	0	− 936	− 1,753	− 2,767	− 3,953	− 5,297
O_2 (g)	0	0	− 2,119	− 3,779	− 5,766	− 8,031	− 10,544
CO (g)	− 26,416	− 32,808	− 45,620	− 51,509	− 57,712	− 64,179	− 70,883
CO_2 (g)	− 94,052	− 94,260	− 97,552	−100,076	−103,100	−106,557	−110,404
H_2 (g)	0	0	− 1,995	− 3,536	− 5,373	− 7,458	− 9,765
H_2O (g)	− 57,798	− 54,636	− 51,713	− 51,490	− 51,657	− 52,167	− 52,987
S_2 (g)	+ 29,860	+ 18,184	− 3,819	− 13,487	− 23,509	− 33,822	− 44,395
SO_2 (g)	− 70,960	− 71,790	− 76,244	− 79,253	− 82,777	− 86,744	− 91,114
SO_3 (g)	− 94,450	− 88,520	− 82,736	− 82,240	− 82,539	− 83,547	− 85,201
H_2S (g)	− 4,815	− 7,892	− 15,552	− 19,604	− 24,087	− 28,952	− 34,167
Na_2O (s)	− 99,400	− 90,000	− 77,210	− 73,395	− 69,996	− 66,906	− 64,055
Na_2CO_3 (s)	−270,300	−250,400	−225,943	−220,060			
Na_2CO_3 (l)					−216,314	−214,798	−214,554
Na_2S (s)	− 89,200	− 86,600	− 88,330	− 91,264			
Na_2S (l)					− 95,061	−100,284	−107,024
Na_2SO_4 (sII)	−330,900	−302,780					
Na_2SO_4 (sI)			−266,906	−257,255			
Na_2SO_4 (l)					−249,650	−244,554	−240,977
NaOH (s)	−101,990	− 90,958					
NaOH (l)			− 78,641	− 76,244	− 74,669	− 73,775	− 73,472
Na_2 (g)	+ 33,970	+ 24,850	+ 6,941	− 1,141	− 9,583	− 18,322	− 27,321

From these values the free energy changes of the furnace reactions have been calculated and these are shown in Table III. The equilibrium constants of the furnace reactions have been calculated according to the well-known formula

$$\Delta F = - RT \ln K = -2.303RT \log K$$

and the values of log K are collected in Table IV.

The following reactions were considered:

[1] C (graphite) + $\frac{1}{2}O_2$ = CO
[2] CO + $\frac{1}{2}O_2$ = CO_2
[3] C (graphite) + O_2 = CO_2
[4] H_2 + $\frac{1}{2}O_2$ = H_2O
[5] $\frac{1}{2}S_2$ + O_2 = SO_2
[6] SO_2 + $\frac{1}{2}O_2$ = SO_3
[7] H_2 + $\frac{1}{2}S_2$ = H_2S
[8] Na_2O (s) + CO_2 = Na_2CO_3 (s, l)
[9] Na_2S (s, l) + $2O_2$ = Na_2SO_4 (sII, sI, l)
[10] Na_2S (s, l) + $\frac{3}{2}O_2$ + CO_2 = Na_2CO_3 (s, l) + SO_2

TABLE III

FREE ENERGY CHANGES OF REACTIONS
(in calories)

Reaction No.	Temperature, °K.					
	298.16	800	1000	1200	1400	1600
[1]	− 32,808	− 43,625	− 47,866	− 52,062	− 56,219	− 60,314
[2]	− 61,452	− 50,996	− 46,814	− 42,621	− 38,425	− 34,224
[3]	− 94,290	− 94,620	− 94,680	− 94,683	− 94,644	− 94,538
[4]	− 54,636	− 48,658	− 46,064	− 43,401	− 40,702	− 37,950
[5]	− 80,882	− 72,215	− 68,730	− 65,256	− 61,802	− 58,372
[6]	− 16,730	− 5,432	− 1,097	+ 3,121	+ 7,204	+ 11,185
[7]	− 16,984	− 11,647	− 9,324	− 6,959	− 4,583	− 2,204
[8]	− 66,140	− 51,181	− 46,589	− 43,218	− 41,335	− 40,095
[9]	−216,180	−174,338	−158,433	−143,057	−128,208	−112,865
[10]	−141,330	−113,126	−102,304	− 92,281	− 82,654	− 72,424
[11]	− 60,448	− 40,991	− 33,574	− 27,052	− 20,861	− 14,052
[12]	− 22,796	− 3,900	+ 3,166	+ 9,417	+ 15,258	+ 21,694
[13]	− 37,280	− 28,359	− 27,603	− 27,685	− 28,477	− 29,902
[14]	+ 28,860	+ 22,822	+ 18,986	+ 15,533	+ 12,858	+ 10,193
[15]	+ 74,850	+ 61,212	+ 56,128	+ 50,776	+ 45,554	+ 40,441
[16]	+193,384	+170,438	+161,599	+152,474	+143,466	+134,559
[17]	+155,732	+133,347	+124,859	+116,032	+107,347	+ 98,813
[18]	+242,442	+185,145	+163,631	+143,253	+124,266	+105,806
[19]	+120,542	+ 93,361	+ 83,379	+ 73,723	+ 65,051	+ 57,505
[20]	+ 11,822	+ 2,317	− 1,551	− 5,447	− 9,359	− 13,280

TABLE IV

LOGARITHM OF EQUILIBRIUM CONSTANTS OF REACTIONS

Reaction No.	Temperature, °K.					
	298.16	800	1000	1200	1400	1600
[1]	24.047	11.917	10.461	9.482	8.776	8.238
[2]	45.043	13.931	10.231	7.762	5.998	4.675
[3]	69.090	25.848	20.692	17.244	14.774	12.913
[4]	40.047	13.292	10.067	7.904	6.354	5.184
[5]	59.285	19.728	15.021	11.885	9.648	7.973
[6]	12.263	1.484	0.240	− 0.568	− 1.125	− 1.528
[7]	12.449	3.182	2.038	1.267	0.715	0.301
[8]	48.479	13.982	10.182	7.871	6.453	5.477
[9]	158.455	47.626	34.625	26.054	20.014	15.416
[10]	103.591	30.904	22.358	16.806	12.903	9.893
[11]	44.307	11.176	7.337	4.922	3.256	1.919
[12]	16.709	1.065	− 0.692	− 1.715	− 2.382	− 2.963
[13]	27.325	7.747	6.033	5.042	4.445	4.084
[14]	− 21.154	− 6.234	− 4.149	− 2.829	− 2.007	− 1.392
[15]	− 54.863	−16.722	−12.267	− 9.247	− 7.111	− 5.524
[16]	−141.745	−46.560	−35.317	−27.769	−22.396	−18.380
[17]	−114.148	−36.428	−27.287	−21.132	−16.757	−13.497
[18]	−177.704	−50.578	−35.761	−26.090	−19.398	−14.452
[19]	− 88.354	−25.504	−18.222	−13.427	−10.155	− 7.855
[20]	− 8.665	− 0.633	0.339	0.992	1.461	1.814

[11] $Na_2S\ (s, l) + \frac{1}{2}O_2 + CO_2 = Na_2CO_3\ (s, l) + \frac{1}{2}S_2$
[12] $Na_2S\ (s, l) + H_2O + CO_2 = Na_2CO_3\ (s, l) + H_2S$
[13] $Na_2O\ (s) + H_2O = 2NaOH\ (s, l)$
[14] $Na_2CO_3\ (s, l) + H_2O = 2NaOH\ (s, l) + CO_2$
[15] $Na_2SO_4\ (s\text{II}, s\text{I}, l) + CO_2 = Na_2CO_3\ (s, l) + SO_2 + \frac{1}{2}O_2$
[16] $Na_2SO_4\ (s\text{II}, s\text{I}, l) + CO_2 + H_2O = Na_2CO_3\ (s, l) + H_2S + 2O_2$
[17] $Na_2SO_4\ (s\text{II}, s\text{I}, l) + CO_2 = Na_2CO_3\ (s, l) + \frac{1}{2}S_2 + \frac{3}{2}O_2$
[18] $Na_2CO_3\ (s, l) = Na_2 + CO + O_2$
[19] $Na_2S\ (s, l) = Na_2 + \frac{1}{2}S_2$
[20] $Na_2 = 2Na.$

All substances in the above reactions are gases unless they are followed by (s) or (l) which indicates that they are solids or liquids.

CONSTRUCTION OF THE PHASE DIAGRAMS

The dependent variable in the phase diagrams is the logarithm of the partial pressure of the gas; the independent variable is the logarithm of the partial pressure of oxygen in the equilibrium mixture, each diagram representing the state of affairs at one temperature.

To be able to derive quantitative relations between the variables, some assumptions on the relative amounts of the reacting substances were necessary. In the following calculations the formula of a gas enclosed in parentheses stands for the partial pressure of the gas in atmospheres.

(1) $(CO) + (CO_2) = 0.15$ atm.
(2) $(H_2) + (H_2O) = 0.10$ atm.
(3) $(H_2S) + (SO_2) + (SO_3) + \frac{1}{2}(S_2) \leqslant 0.01$ atm.
(4) Na is present in excess over S, so that theoretically it would be possible to convert all sulphur present in the waste liquor to Na_2SO_4 or Na_2S.

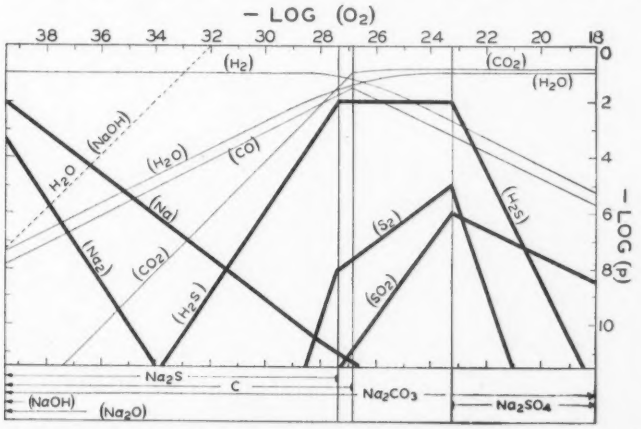

FIG. 1. Condensed phases and partial pressures of gases at 800°K. The small regions where Na_2O and NaOH can exist lie just outside the left margin of the diagram. In the central portion of the diagram there exists a region where all sulphur present will be in the gas phase, mainly as H_2S.

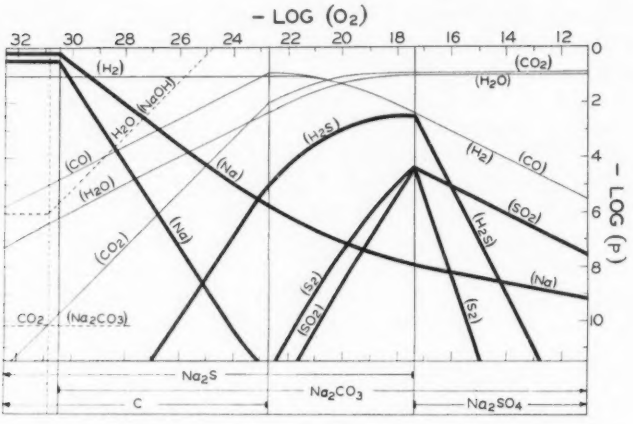

FIG. 2. Condensed phases and partial pressures of gases at 1000°K. NaOH and Na_2O cannot exist at this or higher temperatures.

These are essentially equivalent to the assumptions made by Sillen and Andersson (13) and are close to the actual conditions found in the combustion of calcium-base liquor by Scholander (11). However, even a relatively large error in these assumptions would not influence the result of the calculations too severely.

The phase diagram at 1000°K. was constructed as follows. The partial pressures of CO and CO_2 were found by solving the simultaneous equations

$$(CO) + (CO_2) = 0.15,$$
$$\log (CO_2) - \log (CO) = \log K_{1000} + \tfrac{1}{2} \log (O_2),$$
$$\text{where } \log K_{1000} = +10.231.$$

These equations are obtained from assumption (1) and from applying the law of mass action to the reaction

$$CO + \tfrac{1}{2}O_2 = CO_2.$$

At low oxygen concentrations incomplete combustion will take place, i.e., solid carbon will make its appearance in the phase diagram. To find the oxygen concentration at which this will take place the reactions

$$C \text{ (graphite)} + \tfrac{1}{2}O_2 = CO,$$
$$\text{and } C \text{ (graphite)} + O_2 = CO_2$$

are considered. For these reactions

$$\log (CO) = 10.461 + \tfrac{1}{2} \log (O_2),$$
$$\log (CO_2) = 20.692 + \log (O_2).$$

These lines will intersect the previously calculated lines for log (CO) and log (CO_2) at the same oxygen concentration. Below this concentration solid carbon will be left in the combustion residue.

The reaction equilibrium

$$Na_2O + CO_2 = Na_2CO_3,$$
$$\log (CO_2) = -10.182$$

shows that Na_2O will exist only when the CO_2 pressure is less than $10^{-10.182}$ atm. It will be shown, however, that Na_2CO_3 will dissociate into Na, Na_2, CO, and O_2 before such a low CO_2 pressure can be reached. Therefore, Na_2O cannot exist in any region of the phase diagram at 1000°K., although the equilibrium constant is by no means unfavorable.

The reaction

$$Na_2S + 2O_2 = Na_2SO_4,$$
$$2 \log (O_2) = 34.625$$

shows that Na_2SO_4 will be the solid phase when the oxygen pressure is greater than $\log (O_2) = -17.313$, and Na_2S will be the solid phase when the oxygen pressure is smaller. This explains the sharp break in the curves for the partial pressure of the sulphur gases in the phase diagram at this concentration.

The partial pressures of H_2 and H_2O are found by solving the equations

$$(H_2) + (H_2O) = 0.10,$$
$$-\log (H_2) + \log (H_2O) = \tfrac{1}{2} \log (O_2) + 10.067.$$

Considering the dissociation of NaOH according to the reaction

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

it is found that the dissociation pressure of NaOH is greater than the prevailing pressure of H_2O, and hence NaOH will not be formed in any part of the phase diagram at 1000°K. This has been indicated by the dashed line in the upper left-hand corner of the phase diagram. A study of equilibrium constants only would not exclude the possibility of the formation of NaOH.

The partial pressures of the sulphur gases are calculated according to the following relations:

(*a*) *in the Na_2SO_4 region*

$$Na_2SO_4 + CO_2 = Na_2CO_3 + SO_2 + \tfrac{1}{2}O_2$$
$$\log (SO_2) = -12.276 - \tfrac{1}{2} \log (O_2) + \log (CO_2)$$

$$Na_2SO_4 + H_2O + CO_2 = Na_2CO_3 + H_2S + 2O_2$$
$$\log (H_2S) = -35.317 - 2 \log (O_2) + \log (CO_2) + \log (H_2O)$$

$$Na_2SO_4 + CO_2 = Na_2CO_3 + \tfrac{1}{2}S_2 + \tfrac{3}{2}O_2$$
$$\log (S_2) = -54.574 - 3 \log (O_2) + 2 \log (CO_2)$$

(*b*) *in the whole region*

$$SO_2 + \tfrac{1}{2}O_2 = SO_3$$
$$\log (SO_3) = +0.240 + \log (SO_2) + \tfrac{1}{2} \log (O_2)$$

(*c*) *in the Na_2S* region

$$Na_2S + \tfrac{3}{2}O_2 + CO_2 = Na_2CO_3 + SO_2$$
$$\log (SO_2) = 22.358 + \log (CO_2) + \tfrac{3}{2} \log (O_2)$$

$$Na_2S + H_2O + CO_2 = Na_2CO_3 + H_2S$$
$$\log (H_2S) = -0.692 + \log (H_2O) + \log (CO_2)$$

$$Na_2S + CO_2 + \tfrac{1}{2}O_2 = Na_2CO_3 + \tfrac{1}{2}S_2$$
$$\log (S_2) = 14.674 + 2 \log (CO_2) + \log (O_2)$$

Finally the decomposition of Na_2CO_3 to metallic sodium must be considered.

$$Na_2CO_3 = Na_2 + CO + O_2$$
$$\log (Na_2) = -35.761 - \log (CO) - \log (O_2)$$

$$Na_2 = 2Na$$
$$\log (Na) = +0.170 + \tfrac{1}{2} \log (Na_2)$$

When the combined sodium pressure (Na) + (Na_2) reaches 1 atm. all Na_2CO_3 will dissociate into the gas phase, thus causing the sharp breaks indicated in the curves for (Na), (Na_2), (SO_2), (H_2S), and (S_2). Some of these breaks do

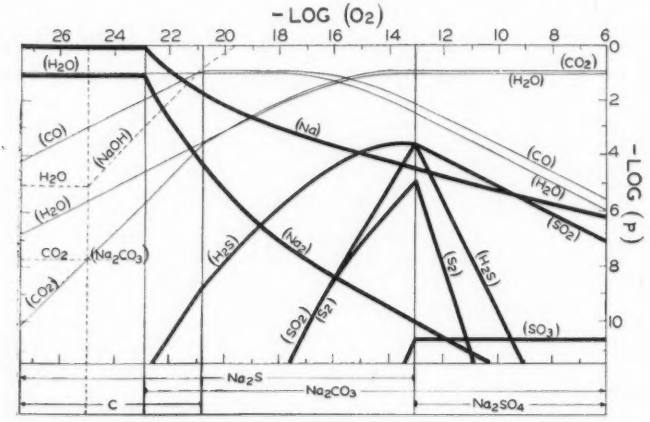

FIG. 3. Condensed phases and partial pressures of gases at 1200°K.

not fall within the region of the phase diagrams drawn in Fig. 2 but may be seen in some of the diagrams for higher temperatures.

The other phase diagrams were constructed in similar manner, using the appropriate equilibrium constants given in Table IV.

The phase diagram at 800°K. is peculiar in having a region where all the sulphur is present in the gas phase and none in the solid (or liquid) phases. This is the result of condition (3) which specifies the amount of sulphur that is present. In this phase diagram there are also regions where Na_2O and NaOH exist as condensed phases although they lie so far in the region of incomplete combustion that they are of academic interest only and are outside the region drawn in Fig. 1.

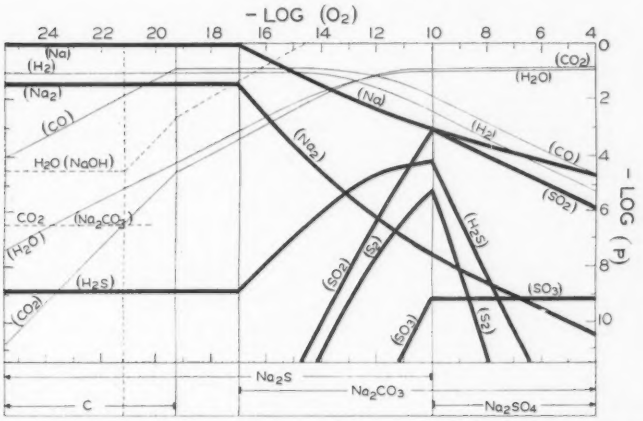

FIG. 4. Condensed phases and partial pressures of gases at 1400°K. The partial pressure of metallic sodium is becoming increasingly important as the temperature increases, and will lead to high fly ash losses.

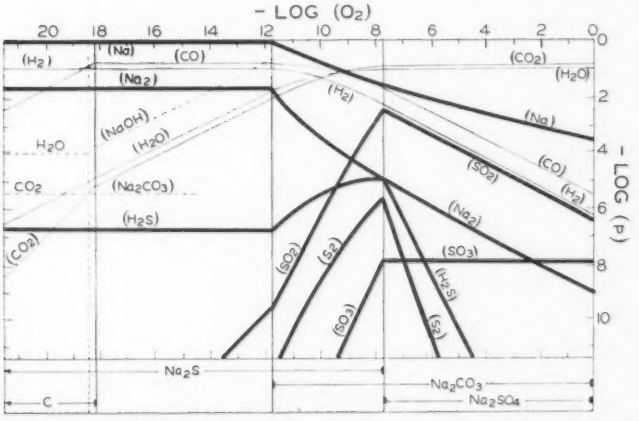

FIG. 5. Condensed phases and partial pressures of gases at 1600°K. The sodium pressure is now so high that the possible region of operation is severely limited.

DISCUSSION

From the phase diagrams it may be seen that Na_2SO_4 can be obtained as an end product at all temperatures investigated if there is an excess of oxygen. However, sulphur bound as sulphate is lost as far as chemical recovery is concerned. In the burning of kraft liquor, for example, the desirable sulphur compound for recovery is Na_2S. It may be seen from the diagrams that Na_2S

may be obtained as the main sulphur compound if the waste liquor is burned in a deficiency of air. If the delta function of Sillen and Andersson is applied in this case,

$$\Delta/100 = (O_2) - \tfrac{1}{2}(H_2) - \tfrac{1}{2}(CO)$$

where Δ is approximately the excess or deficiency of oxygen beyond that for complete combustion of the waste liquor, Fig. 6 may be constructed. The solid lines in Fig. 6 indicate the regions in the Δ–T plane where more than 99% of the total sulphur present in the waste liquor will exist as that sulphur com-

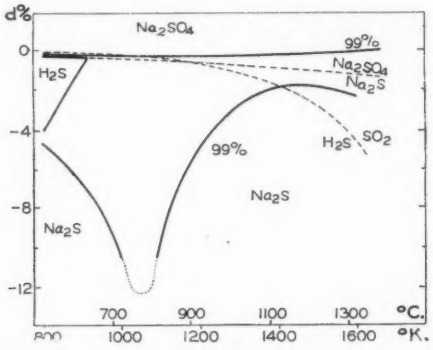

FIG. 6. Compounds obtained at various temperatures and oxygen deficiencies.

pound labelling the region (Na_2SO_4, Na_2S, or H_2S). Within the area bounded by these lines and not labelled, the sulphur will be distributed in varying proportions between the gas and the condensed phases. The dashed lines indicate the equilibrium lines between Na_2SO_4 and Na_2S, and between SO_2 and H_2S. The amounts of S_2 and SO_3 formed are negligible over the whole range investigated.

Study of the diagrams reveals that the most favorable operating conditions will be near 1400°K. (1127°C., 2061°F.) and at an oxygen deficiency of about 2%. At lower temperatures either the sulphur loss will be too high or the region of incomplete combustion is reached. At higher temperatures the sodium loss will become excessive. Even at 1400°K. the vapor pressure of metallic sodium is rather high, which is in agreement with the high alkali fly ash loss generally experienced in kraft furnace operation. The metallic sodium will, of course, recombine with the stack gases as soon as the temperature falls, and only about 1 part in 10,000 would remain uncombined when the temperature has fallen 400°C. below the reaction temperature.

Other sulphur compounds might be formed during cooling of the phases after the reaction. Hence, quick separation of gases and ash and rapid cooling of the ash will avoid this complication.

No thermodynamic data are available on the solutions of the molten smelt, and this effect had, therefore, to be ignored completely. Solutions of such highly

polar compounds as Na_2S will certainly be far from ideal but, as the equilibrium constants of the reactions under consideration change quite rapidly with temperature, this omission will not have too serious an effect. The effect may be thought of as causing a 'temperature' error, and thus even a very strong solution effect might shift the optimum operating temperature as little as 50°C.

REFERENCES

1. BENTON, A. and INATOMI, T. H. J. Chem. Phys. 29: 1946–1948. 1952.
2. FRIEDRICH, K. Metall u. Erz, 11: 85–, 196–. 1914. (*Quoted in* Ref. 10.)
3. KELLEY, J. C. R. and SNYDER, P. E. J. Am. Chem. Soc. 73: 4114–4115. 1951.
4. KELLEY, K. K. U. S. Bur. Mines Bull. 393. 1936.
5. KELLEY, K. K. U. S. Bur. Mines Bull. 476. 1949.
6. KELLEY, K. K. U. S. Bur. Mines Bull. 477. 1950.
7. LANDIYA, N. A. Zhur. Fiz. Khim. 24: 257–260. 1950.
8. LATIMER, W. M. The oxidation states of the elements. 2nd ed. Prentice-Hall, Inc., New York, N.Y. 1952.

9*a*. MAY, M. N. Tappi, 35: 511–517. 1952.

9*b*. MAY, M. N. Doctoral dissertation. The Institute of Paper Chemistry, Appleton, Wisconsin. 1952.

10. ROSSINI, F. D., WAGMAN, D. D., EVANS, W. H., LEVINE, S., and JAFFE, I. Selected values of chemical thermodynamic properties, U. S. National Bureau of Standards, Circular 500. U. S. Government Printing Office, Washington, D.C. 1952.
11. SCHOLANDER, A. Tappi, 35: 1–4. 1952.
12. SHOMATE, C. H. J. Am. Chem. Soc. 66: 928–929. 1944.
13. SILLEN, L. G. and ANDERSSON, T. Svensk Papperstidn. 55: 622–631. 1952.

THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XXIII. THE EFFECT OF FLOW CONFIGURATION: *n*-PENTANE AND ACETALDEHYDE IN COMBUSTION TUBES OF VARIOUS MATERIALS[1]

By R. O. King,[2] S. Sandler,[3] and R. Strom[4]

ABSTRACT

The experiments presently described are the first of a series intended to elucidate the effect of flow configuration on the velocities of oxidation and decomposition reactions in fuel vapors and gases and on the temperatures of ignition of their mixtures with air. A beginning is made in this Part by describing the effect of flow configuration on the oxidation and ignition of mixtures with air of *n*-pentane and acetaldehyde in a simple form of reactor, namely a combustion tube of large diameter relative to its length. Experiments were made with tubes of materials similar to those in the combustion chambers of engines. The tubes were approximately 1 in. internal diam. and were supported concentrically in a 2 in. diameter vertical furnace with their ends protruding 3 in. from it. There were then steep temperature gradients extending from the midsection of maximum temperature to the relatively cool ends. The combustible gaseous mixture supplied to the lower end of the tube ascended along the wall in a boundary layer approximately 3 to 4 mm. thick and on arriving at the midsection, changed direction, and in large part descended as a central stream which reversed in direction on arriving at the cooler part of the tube adjacent to the lower end of the furnace and then joined the ascending boundary layer. Random turbulence existed between the ascending and descending streams and caused some interchange of gaseous mixture. The convection circulation in the upper part of the tube comprised a descending boundary layer and a central stream ascending to the exit. There was a length of random turbulence between the upper and lower circulations. When the combustion tube was of mild or stainless steel, the velocity of surface oxidation reactions increased as the temperature was raised with the products tending to be carbon dioxide and steam only, and the inflammability of the boundary layer diminished accordingly. Now, because the mixture supplied to the tube goes to the boundary layer its inflammability will increase and its ignition temperature decrease as the rate of mixture supply is increased. Thus when a correct pentane–air mixture was supplied at 100 cc./min. ignition did not occur but on increasing the supply to 200 cc./min. there was explosive ignition at 670° C. Ignition occurred at still lower temperatures on continuing to increase the rate of mixture supply. It occurred at 589° C. when the rate was 475 cc./min. Somewhat higher temperatures were required for ignition in the same circumstances when using a mild steel tube or correct acetaldehyde–air mixtures. When the tube was of carbon or graphite, ignition did not occur even when temperatures were higher than 750° C. and the tubes were being consumed by flameless combustion. The occurrence of ignition in a low-temperature range and again in a high-temperature range is of especial interest in respect of reaction kinetics. The double effect was obtained with either pentane or acetaldehyde in vitreous tubes, but when light metal tubes were used, ignition occurred in the high-temperature range only, with pentane, and in the low-temperature range only, with acetaldehyde. When using a silica tube, ignition of a correct pentane–air mixture occurred in the low-temperature range at 325° C., a temperature at which aldehyde is formed in great profusion by the oxidation of the pentane. When acetaldehyde–air mixtures were used, the preliminary oxidation to aldehyde was not required and ignition in the low-temperature range occurred at 250° C. The respective high-temperature igni-

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tions occurred at 530 and 500° C. Pentane did not oxidize readily to aldehyde in an aluminum tube and ignition occurred in the high-temperature range only, at 646° C., for a correct mixture, but with acetaldehyde, a low-temperature ignition occurred at 364° C. and ignition was not obtained at high temperatures. As a result of these experiments it is concluded that ignition in the high-temperature range, of mixtures with air of either pentane or acetaldehyde, is an effect which depends on the inflammability of the boundary layer and the temperature of the surface over which it is passing. As a further result of the experiments a working hypothesis is advanced for the cause of ignition in the low-temperature range. It is that the reaction leading to ignition is initiated by the peroxides formed after aldehyde has been carried from the boundary layer into the central stream. Whether ignition then obtained was a result of a chain reaction starting from the aldehyde peroxide or a result of nuclei of ignition being formed on the decomposition of the peroxide is an open question. The nuclear theory appears to be the more probable, according to comparable engine experiments.

I. INTRODUCTION

The first experiments on flow configuration, so far as we know, were made by Count Rumford (13), who demonstrated by experiment that the liquid in a vertical glass tube was set in motion as its temperature was raised by heat from an external source, applied *uniformly* over the length of the tube. The motion set up a flow configuration comprising an ascending stream along the wall of the tube and a contraflow along the vertical axis. On the withdrawal of the source of heat the streams reversed in direction as the liquid cooled. Thus was initiated the concept of the transfer of heat by convection; a phenomenon not in agreement with the then-current caloric fluid theory of heat.

The Rumford flow configuration was made visible by the use of a suspension of powdered amber in water, stabilized by the water being brought to the same density as the amber by a suitable addition of caustic soda. The highest temperature of the heat source was that of boiling water and no reaction occurred in the liquid that would liberate or absorb heat. When the temperature of the liquid became equal to that of the uniformly heated wall the previously observed flow configuration disappeared. There would however always be a flow configuration set up by heat convection if the wall temperature were not uniform or if, being uniform, the tube contained a combustible gaseous mixture and heat were liberated by an oxidation reaction occurring on its surface. The tube would then become a reactor such as is commonly used for the study of reaction kinetics by what are described briefly as the "bulb" and "flow" methods.

The bulb method.—The combustible mixture is contained in a closed vessel whose surface is heated uniformly as the temperature is raised to initiate reaction. The observed rate of the increase of pressure, due to the reaction, is taken to indicate the rate of the reaction. There will be a flow configuration in the vessel, due to heat convection while the temperature is being raised, and even if the temperature be held constant, the heat liberated by continuing surface oxidation reactions will maintain circulating convection currents. When the experiment is repeated after the vessel has been packed with fragments of its material in order greatly to increase surface area, it is generally found that rate of reaction is reduced, sometimes nearly to zero. It is com-

monly believed that relative values for rates of surface and gas phase reactions can thus be obtained. It is indicated however by experiments described in Part II (5) that reaction in the unpacked vessel occurred in whole or in large part, depending on the nature of the reacting substance, on the heated surface and tended to be inhibited by its own products when the flow configuration was destroyed by packing. The pattern and the magnitude of the flow configuration in a closed reactor would vary with the ratio of surface area to volume, the volume, and geometrical conformation. Reaction rates determined by the closed vessel (bulb) method are known to vary accordingly. Thus the method does not, as is generally supposed, enable a distinction to be made between surface and gas phase reactions.

The flow method.—The combustible mixture is supplied continuously to the reactor and the process of raising its temperature by heating the wall of the tube is also continuous. Heat is transferred from the wall to the mixture mainly by circulating convection currents. The corresponding flow configuration becomes stable for any particular temperature level and the corresponding rate of oxidation can be determined by analysis of the exit gases. Experiments with various forms of reactor were described in Part II (5). The flow configuration due to heat convection was varied by changes in the form of the reactor and the ratio of surface area to volume. In some cases it was created in part and in others entirely by passing the reactant through a small orifice into a reactor of relatively small volume, thus forming a flow configuration of the nature of a toroidal vortex. Rates of oxidation observed when using the vortex type of flow configuration were remarkably high and pentane in mixtures with air could be completely oxidized without ignition in a reactor of Jena glass. Further experiments made when using the toroidal vortex type of reactor are described in Part VII (6). The experimental results supported the conclusion that flow configuration is a major factor influencing the velocities of oxidation reactions and corresponding temperatures of ignition.

The Flow Configuration in the Reactors Used for the Experiments of This Part

The experiments were carried out by the flow method and with tubular reactors, described hereafter as combustion tubes. They were always approximately one inch in internal diameter and supported concentrically in a vertical tubular electric furnace of 2 in. internal diameter with their ends protruding about 3 in. The heating coil of the furnace was wound uniformly and was $6\frac{1}{2}$ in. long. The annular space between the furnace wall and the combustion tube was closed at both ends by tightly fitted transite washers. The arrangement ensured steep temperature gradients along the heated tube from the midsection of maximum temperature to the relatively cool ends as shown by the graphs of Fig. 1. It will be noted that the position of maximum wall temperature varies somewhat with the heating current but that it is approximately one inch above the middle section of the length within the furnace.

The gaseous mixture as it passes slowly through the lower part of the tube tends to be heated to the maximum wall temperature and thereafter cooled on passing through the upper part of progressively diminishing temperature

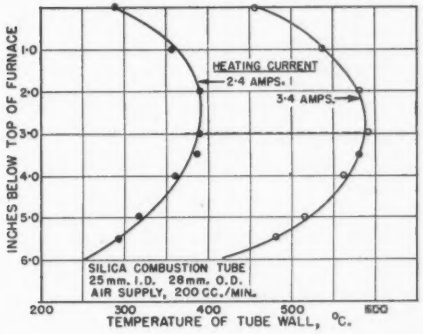

FIG. 1. Temperature gradients along the wall of a silica tube as mounted in the electrically heated furnace.

to the exit. The flow configuration would in general, according to Rumford's experiments, comprise a circulating convection current with a descending central stream in the lower part of the tube and a convection circulation in the opposite direction in the upper part. A more precise knowledge of the flow configuration in the particular combustion tubes used for the experiments was required, especially in respect of the position of the circulations and of the motions which must exist within them.

The pattern of the flow configuration became visible on continuously passing nitrogen containing a small concentration of iron carbonyl through one of the transparent combustion tubes heated electrically by means of an open winding of nichrome strip. The carbonyl decomposed to deposit iron on surfaces at a suitable temperature as would be expected from Callendar's experiments (2). The deposit extended over the entire heated length of the tube at temperatures below 300° C. It is probable that all of the iron in the carbonyl could then have been recovered in the same manner that nickel can be recovered quantitatively from the carbonyl. As the temperature of the midsection of the tube was increased, the tendency of the iron from the carbonyl to deposit thereon diminished. At a maximum tube temperature of 500° C. the deposit remained on the cooler ends only. It could then be seen that the gas in the tube was impregnated with fine particles and tiny flakes of iron, which in spite of their relatively high density were carried by the convection currents to form a pattern of the flow configuration.

The particles in the ascending stream of gas were seen to rise to above the position of maximum tube temperature, then to move toward the longitudinal axis and descend in a well-defined stream to the cooler lower position. The particles did not drop out when the convection current reversed in direction. They either adhered to the surface onto which they were carried or if extremely fine were carried upward by the ascending stream. The thickness of this stream, as estimated by visual observation, appeared to vary from 3 to 4 mm.

A convection circulation was seen to be formed in the upper part of the tube,

near the top of the furnace. This circulation comprised an ascending central stream and a descending stream along the tube wall but was less well defined than that of the reverse circulation below the position of maximum tube temperature.

The experiments indicated that random turbulence prevailed in the spaces between the ascending and descending streams of gas and in the length of tube between the upper and lower convection circulations.

The Combustion Tubes Used as Reactors for the Experiments

The first experiments on flow configuration as described in this part were carried out with combustion tubes of materials similar to those present in the combustion chambers of engines with the object of determining the temperatures at which their surfaces would ignite the fuel–air mixture. The tubes were not obtainable of materials precisely the same as those used in the engine but it was considered that the purpose of the experiments would be served by using generally similar materials, namely, stainless steel (18–8 Cr–Ni) to represent exhaust valve material; silica, vycor glass (96% silica), and Pyrex glass to represent the materials of spark plug cores; mild steel, aluminum (97% Al), and magnesium (92% Mg) to represent piston material; carbon and graphite to represent carbonized surfaces. Tubes of the materials mentioned were not obtainable always of the same internal diameter and wall thickness and these dimensions were as given below for the tubes used for the experiments.

Tube material	Internal diameter	Wall thickness	Tube material	Internal diameter	Wall thickness
Stainless steel	28 mm.	1.58 mm.	Aluminum	28 mm.	1.58 mm.
Mild steel	28 mm.	1.58 mm.	Magnesium	28 mm.	1.05 mm.
Silica	25 mm.	1.58 mm.	Graphite	25 mm.	6.4 mm.
Vycor glass	19 mm.	3.2 mm.	Carbon	25 mm.	6.4 mm.
Pyrex	28 mm.	1.58 mm.			

Methods of Measurement and Presentation of Experimental Results

The methods used for the measurement of temperature and the proportion of combustible vapor in the mixtures with air, and for obtaining and analyzing samples of the products of pre-explosion combustion are described in an appendix.

Stoichiometric mixtures are described as "correct" and others as per cent weak or rich according to the percentages by which the combustible vapor is less or more than required for the correct mixture. This mixture contains approximately $2\frac{1}{2}\%$ by volume of pentane vapor or 8% by volume of acetaldehyde vapor. Rates of supply of mixture to the combustion tube are given in terms of the rates of air supply.

The *n*-pentane was supplied by Phillips Petroleum Co. and the acetaldehyde by the Eastman Kodak Company. Both substances were of Technical grades but were purified by redistillation before use.

The experimental work is described in four sections. Preliminary experiments described in the first were made with combustion tubes of the nine varieties of material in order to determine respective explosive ignition temperatures, denoted hereafter by the abbreviation "E.I.T.". It was disclosed by these

experiments that, excluding the carbon and graphite tubes in which ignition did not occur, the obtaining of significant experimental results required the use of three varieties only of tube material, namely steel, aluminum, and silica. Experiments made accordingly are described in the respective sections III A, B, and C. A discussion of experimental results, given in Section IV, suggests that the reactions which lead to ignition of paraffin hydrocarbons in the gaseous phase are dependent on the formation of aldehyde peroxides (peracids and diacyl peroxides).

II. PRELIMINARY EXPERIMENTS

The Influence of a Variety of Surfaces on Igniting Temperature

The preliminary experiments were carried out with the object of determining the relative effects of the surfaces of the nine available varieties of combustion tube material on the ignition of correct mixtures with air of pentane and acetaldehyde when supplied at 200 cc./min. This rate was selected because when using the steel combustion tubes and lower rates of mixture supply, surface oxidation of the pentane or the acetaldehyde to final products was nearly completed without the occurrence of ignition. It was not possible, for example, to ignite correct mixtures in these tubes when rate of mixture supply was as low as 100 cc./min.

The surface temperatures required for explosive ignition of correct mixtures in the conditions of the experiments are given in Table I. Ignition is described

TABLE I

TEMPERATURES OF EXPLOSIVE IGNITION OF CORRECT MIXTURES WITH AIR OF PENTANE OR ACETALDEHYDE SUPPLIED AT 200 CC./MIN.

Tube material	Combustible substance	Temperature of explosive ignition
Stainless steel	Pentane	670° C., 1236° F.
	Acetaldehyde	730° C., 1346° F.
Mild steel	Pentane	644° C., 1190° F.
	Acetaldehyde	685° C., 1260° F.
Aluminum	Pentane	646° C., 1195° F.
	Acetaldehyde	364° C., 786° F.
Magnesium	Pentane	615° C., 1139° F.
	Acetaldehyde	349° C., 660° F.
Silica	Pentane	496° C., 926° F.
	Acetaldehyde	237° C., 459° F.
Vycor glass	Pentane	539° C., 1002° F.
	Acetaldehyde	246° C., 475° F.
Pyrex glass	Pentane	493° C., 920° F.
	Acetaldehyde	241° C., 466° F.
Graphite	Pentane	Temperatures taken to 750° C. (1382° F.) without explosion
	Acetaldehyde	
Carbon	Pentane	Temperatures taken to 760° C. (1400° F.) without explosion
	Acetaldehyde	

as explosive when it is accompanied by a flame with rapid burning of the combustible mixture to final products. The nonexplosive type leads merely to partial burning even of correct mixtures and is generally accompanied by "cold" flames. The effect is indicated by pressure oscillations in the mixture flow system, not by a single sharp rise.

Comments on Data of Table I

Stainless and mild steel tubes.—The temperatures of explosive ignition recorded in Table I are higher for the acetaldehyde–air mixtures than for the pentane–air mixtures by margins of 60° C. and 41° C. in the stainless and mild steel tubes respectively. This, in view of recorded igniting temperatures, was an unexpected result. The temperature at which explosive ignition occurs in steel tubes varies with the surface state; a factor depending on the time of use at particular temperatures and the concentration of oxygen in the reacting mixture.

Aluminum and magnesium tubes.—The thermal conductivity of either of the light metals is several times greater than that of steel. It was consequently necessary to fit small water-cooled metal coils to the ends of the combustion tubes protruding from the furnace in order to obtain temperature gradients over the length within the furnace comparable with those along the steel and vitreous tubes. Explosive ignition of the pentane–air mixture occurred at approximately the same temperature as in the mild steel tube, but the acetaldehyde–air mixture exploded in the aluminum tube at temperatures approximately 200° C. lower than in the mild steel tube. The explosion temperatures of 646° C. and 615° C. for the pentane–air mixture are little lower than the respective melting points of the pure metals, 660° C. for aluminum and 651° C. for magnesium. The magnesium tube itself ignited and burned on an occasion when the heating current was not switched off immediately after observing an ignition temperature of 615° C. for a pentane–air mixture.

Vitreous tubes.—The pentane–air mixture ignited and exploded at a temperature of 496, 539, and 490° C. in the silica, vycor, and pyrex tubes respectively. There were, however, slight pressure oscillations accompanied by some luminescence in the temperature range 280 to 320° C., that is, ignition in this lower temperature range was not explosive in the conditions of the experiments. The acetaldehyde–air mixture ignited and exploded at temperatures of 237, 246, and 241° C. in the silica, vycor, and pyrex tubes respectively. An explosive ignition temperature of 240° C. can be taken as an average value. It will be shown later that ignition was nonexplosive for mixtures weaker than correct and that there is another and higher range of temperature over which ignition is explosive for mixtures varying from weak to rich.

Graphite and carbon tubes.—Combustion of the tube material, as indicated by the formation of carbon dioxide in appreciable quantity when air only was passed through the tubes, began at 600° C. and 400° C. for the graphite and carbon tubes respectively. Neither the pentane nor the acetaldehyde mixtures with air ignited when passed through the tubes at the temperatures mentioned. An attempt was made to obtain ignition by raising the temperatures of the graphite and carbon tubes to 750 and 760° C. respectively but was not success-

ful although the tubes were red hot and burning by flameless combustion. The failure is reminiscent of Davy's finding, as quoted by Jost (4, p. 25), that "firedamp (methane) cannot be ignited by flameless burning charcoal". Further experiments with these combustion tubes will be described in a subsequent Part.

Combustion Tube Materials for Further Experiments

The experimental results given in Table I show that similar igniting effects were obtained with silica, vycor, or pyrex tubes, with aluminum or magnesium tubes, and with two varieties of steel tubes. It was considered therefore that the significance of further experiments would not be impaired if combustion tubes of only three varieties of material were used. The varieties selected accordingly were silica, aluminum, and steel.

III. EXPERIMENTS ON THE OXIDATION AND IGNITION OF ACETALDEHYDE AND PENTANE AS AFFECTED BY RATE OF MIXTURE SUPPLY AND MIXTURE STRENGTH

A. Silica Combustion Tube Experiments

Marcel Prettre (10, 11, 12) was the first to demonstrate by experiment that ignition of mixtures with air of acetaldehyde or of pentane and higher normal paraffins could occur in two temperature stages. It is indicated accordingly that the average values of 237 to 246° C. given in Table I for the explosion of correct mixtures with air of acetaldehyde in vitreous combustion tubes are for first-stage low-temperature ignitions and that relatively high values of 493 to 539° C. given for the explosive ignition of correct pentane–air mixtures are for second stage ignitions.

Prettre used horizontal reaction vessels 120 to 150 mm. long and 60 mm. diam., maintained at a uniform temperature by being placed in mid-position in a long electric furnace. The reacting mixture entered and left the vessel through long capillaries. Thus his experimental method was radically different, especially in respect of the factor of flow configuration, from the combustion tube method used for the experiments described in this Part. It was therefore of interest in respect of reaction kinetics to find out whether ignition would occur in two temperature stages for oxidation reactions in combustion tubes arranged as for the experiments described in Section II.

The silica combustion tube used for experiments with acetaldehyde was 25.0 mm. in internal diameter and had been used for the preliminary experiments of Section II. The tube used for the experiments with pentane was 26.0 mm. in diameter and was new. Air was always supplied at 200 cc./min. and mixture strength was varied by suitable additions of vaporized acetaldehyde or pentane.

Ignition Experiments with Acetaldehyde

First Stage Ignition

Explosive ignition of a correct acetaldehyde–air mixture occurred at 260° C. That is at 23° C. higher than given earlier, Table I. The difference is not significant and must be disregarded because surface action changes in an

unpredictable manner with time of use and other factors and temperatures of ignition vary accordingly. Little change of E.I.T. occurred as mixture strength was increased to 40% rich. Ignition was nonexplosive for mixtures weaker than correct as indicated by the broken line of graph A, Fig. 2, and was not obtainable with mixtures leaner than 50% weak. Oxidation was always accompanied by luminosity before and after ignition in the low-temperature range.

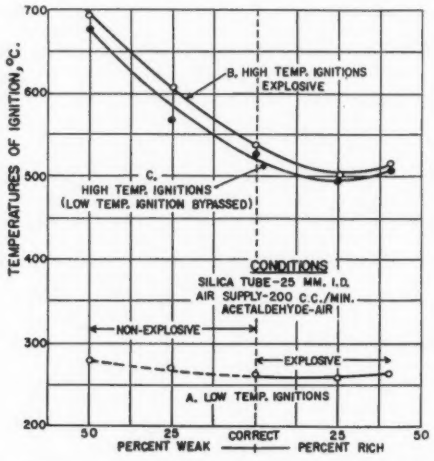

FIG. 2. Ignition characteristics of acetaldehyde–air mixtures in a silica combustion tube.

Second Stage Ignition

The mixtures with air remained luminous as temperature was raised after the occurrence of a first stage ignition. The accompanying slight pressure oscillations disappeared at temperatures approximately 100° C. lower than that of the second stage ignition of a correct mixture. Second stage ignition was always explosive and without premonitory pressure oscillations. The observed values of E.I.T. are given by graph B of Fig. 2. The large variation of E.I.T. with change of mixture strength for mixtures weaker than correct will be noted. Thus E.I.T. was 700° C. for a mixture 50% weak and 540° C. for the correct mixture.

The method of experiment was such that high-temperature ignition might be attributed to the reduction of the inflammability of the mixture due to dilution with combustion products of the previous low-temperature ignition, although temperature was raised slowly after a first stage ignition in the expectation that products of combustion would be cleared from the tube before the occurrence of a high-temperature ignition. It appeared, nevertheless, that confirmatory experiments should be made. The temperature of the tube was therefore raised slowly to 400° C. while air only was passed through it. Acetaldehyde was then supplied at the rate required for a correct mixture and

no explosion occurred until the temperature was increased further to 530° C. High-temperature explosions were obtained in the same manner for mixture strengths of the range of the experiments. The experimental results are exhibited by graph C of Fig. 2. It will be noted that explosive ignition temperatures obtained by the different experimental procedures are in close agreement.

Ignition Experiments with Pentane

First Stage Ignition

The effect was obtained for mixture strengths ranging from 25% weak to 100% rich. It occurred after a period of slowly rising temperature during which faint luminescence could be seen, and was indicated by a single small but distinct pressure "blip", accompanied by the passage of a "cool" flame through the mixture. The nonexplosive first stage ignition temperatures thus determined are given by the broken line graph A of Fig. 3. The temperature of the effect was 325° C. for 25% weak and correct mixtures. It diminished by 15° C. only over the mixture range 25% weak to 100% rich.

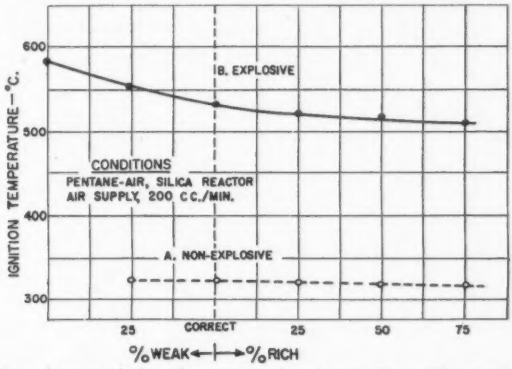

FIG. 3. Ignition characteristics of pentane–air mixtures in a silica combustion tube.

When the tube temperature was raised, luminescence and passages of cool flames continued but with decreasing intensities. The cool flames moved slowly and were not accompanied by pressure oscillations sharp enough to be indicated by the manometer. It was therefore not possible to determine the range of temperature of the first stage of ignition at any particular mixture strength.

Second Stage Ignition

Ignition was explosive over the range of mixture strength used for the experiments, namely 50% weak to 100% rich. Values of E.I.T. are given by graph B, Fig. 3. The E.I.T. for a correct mixture was 535° C. The value observed earlier, Table I, when a different silica tube was used, was 496° C. The experimental results, graph B of the figure, show that E.I.T. increased by 50° C. on the weak side of correct mixture and decreased by 25° C. on increasing mixture strength from correct to 100% rich.

Temperatures of the First and Second Stage Ignition as Affected by Mixture Strength

The graphs of Figs. 2 and 3 show that the temperature of either explosive or nonexplosive first stage ignition of mixtures with air of acetaldehyde or pentane in silica tubes is nearly independent of mixture strength. On the other hand, the temperature of the always explosive second stage ignition of the acetaldehyde increased from 540° C. to 700° C. as mixture strength was reduced from correct to 50% weak. The temperature of the second stage ignition of pentane increased from 520° C. to 585° C. in the same circumstances.

Comparison of Second Stage Ignition Temperatures as Given by Figs. 2 and 3 with Those Given by Prettre

It is somewhat remarkable that the graphs of Fig. 2, for the temperatures of the two stage ignition of acetaldehyde, are similar to those given by Prettre (11) for the two stage ignition of pentane. Thus Prettre found that the first and second stage ignitions of a correct pentane–air mixture occurred at 260° C. and 525° C. respectively. The corresponding temperatures determined by the tube method for a correct acetaldehyde–air mixture were 260° C. and 530 to 540° C., Fig. 2.

The Relation between Wall Temperature and Rate of Oxygen Reacted, Acetaldehyde and Pentane Mixtures with Air

Rates of oxygen reacted as a silica tube was heated to the temperature required for the second stage of ignition of acetaldehyde in three concentrations in mixtures with air are given by the graphs of Fig. 4, and by those of Fig. 5 for four concentrations of pentane in mixtures with air.

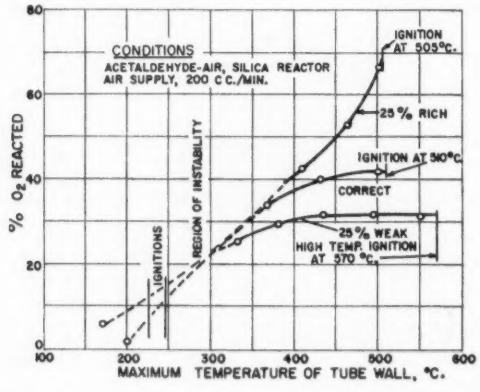

FIG. 4. Percentages of oxygen reacted prior to first and second temperature stages of ignition of acetaldehyde–air mixtures in a silica combustion tube.

Acetaldehyde, Fig. 4

Graphs are given for mixtures 25% weak, correct, and 25% rich. Pressure oscillations of a magnitude to vitiate accurate measurement of rates of acetalde-

hyde supply by the method used began almost immediately after the beginning of the oxidation reaction. The temperature ranges over which accurate measurements could not be made are shown by the breaks in the graphs.

Considering the higher temperature range over which pressure oscillations did not occur and taking r = rate of oxygen reacted, then $dr/dt = 0$ over a temperature range of 130° C. preceding the explosive ignition of the 25% weak mixture at 570° C. When the mixture was correct, $dr/dt = 0$ over the temperature range of approximately 30° C. only, preceding second stage ignition at 520° C. When the mixture was 25% rich, a zero value for dr/dt was never obtained; on the contrary the ratio increased rapidly with increase of temperature and attained the high value of 0.37% of oxygen reacted per ° C. prior to second stage ignition at 505° C.

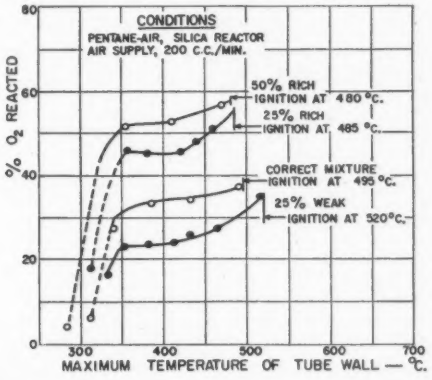

FIG. 5. Percentages of oxygen reacted prior to the second stage ignition of pentane–air mixtures in a silica tube.

Pentane, Fig. 5

The graphs of the figure differ from those of Fig. 4 for acetaldehyde, in that the initial rate of oxidation increases with great rapidity over the temperature range extending to approximately 350° C. Experimental points within this range were not obtained because of the difficulty of accurate observation due to pressure oscillations.

The rapid increase in rate of oxidation below 350° C. is commonly attributed to a correspondingly rapid increase in the rate of formation of aldehydes, water, and organic acids, which reaches a maximum at temperatures in the range 350 to 400° C. In other conditions, such as described in Part II (5), rate of oxidation diminished as temperature was further increased; the temperature coefficient of reaction then became negative.

The second stage ignition temperature given by the graph of Fig. 5 for a correct mixture is 495° C. The ignition temperature for a similar mixture given in Table I is 496° C. The second stage ignition temperatures of Fig. 5 are

however not in close agreement with those given by the graph of Fig. 3. These were however obtained when using a new silica tube of an internal diameter of 26.0 mm.

The Effect of Rate of Supply of Correct Mixtures on First and Second Stage Ignition Temperatures

Correct mixtures with air of acetaldehyde and pentane were used for experiments made at four rates of mixture supply, which as before are stated in terms of rate of air supply. The experimental results are tabulated below. These results were obtained with the new 26 mm. diameter silica tube.

The data of Table II show that in the conditions of the experiments, the temperatures of the first stage ignition of correct mixtures with air of either acetaldehyde or pentane were not affected by increasing the rate of correct

TABLE II

THE EFFECT OF RATE OF MIXTURE SUPPLY ON IGNITION TEMPERATURES

	Rate of supply, cc./min., of correct mixtures and ignition temp., ° C.			
	100 cc.	200 cc.	300 cc.	475 cc.
First stage, acetaldehyde	260	262	268	285
Second stage, acetaldehyde	679	558	542	538
First stage, pentane	321	318	318	322
Second stage, pentane	574	532	532	528

mixture supply from 100 to 475 cc./min. and thereby obtaining a corresponding decrease in time of exposure. The small recorded differences of ignition temperature are within the accuracy of experiment.

The data for the temperatures of the second stage of ignition show on the contrary a considerable decrease of ignition temperature for an increase in rate of correct mixture supply of from 100 to 200 cc./min. The decreases were 121° C. and 42° C. for the acetaldehyde and pentane mixtures respectively. A further increase of rate of supply to 475 cc./min. was of small effect on ignition temperatures.

B. Aluminum Tube Experiments

The temperatures of explosive ignition given in Table I are for correct mixtures supplied to an aluminum combustion tube at 200 cc./min. The mixture of pentane with air exploded at 646° C. There was no evidence of a relatively low temperature first stage ignition of the pentane–air mixture. On the other hand, the acetaldehyde–air mixture exploded at the relatively low temperature of 364° C. There was therefore a possibility that a second stage ignition would occur at a considerably higher temperature. An attempt to obtain it was defeated by the melting of the tube.

Effect of Rate of Supply of Correct Mixtures

The values of E.I.T. observed when correct mixtures with air of acetaldehyde and of pentane were supplied to the aluminum tube at 100 to 475 cc./min. are tabulated below.

TABLE III

Rate of mixture supply, cc./min.	E.I.T., ° C.	
	Pentane	Acetaldehyde
100	Nil	375
200	646	364
300	629	362
475	620	382

The rate of mixture supply determines the time of exposure of the reacting mixture to the temperature and flow configuration conditions in the combustion tube. It will be noted accordingly that the E.I.T. of the pentane–air mixture decreased as time of exposure decreased in the same manner but to a lesser extent as rate of supply was increased from 100 to 200 cc./min. A further increase in rate of supply to 475 cc./min. and a corresponding decrease in time of exposure led to an increase in E.I.T. of 20° C.

Temperatures of Explosive Ignition as Affected by Mixture Strength

The experimental results given in Table III are for correct mixtures, with rate of mixture supply as a variable factor. Further experiments were made with a particular rate of supply, namely 200 cc./min., and with mixture strength as a variable. The results are given by the graphs of Fig. 6. It will be noted that the E.I.T. for both pentane and acetaldehyde attained a minimum value for mixtures with air approximately 50% rich; the total variation over the mixture strength range 50% weak to 75% rich was 50° C. for pentane, 65° C. for acetaldehyde.

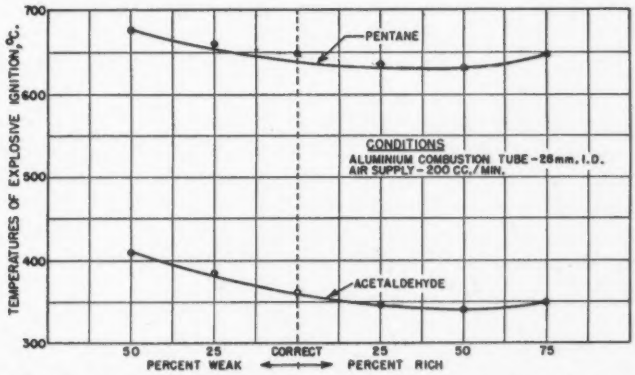

FIG. 6. Explosive ignition temperatures in an aluminum combustion tube as affected by the concentration of acetaldehyde or pentane in mixtures with air.

Ignition of Acetaldehyde in the Aluminum Tube Considered as a First Stage Effect

It was indicated by analyses of samples taken during the experiments made to obtain the data of Table III and of Fig. 6 that the observed ignition temperatures were those of a first stage effect. The temperature of the aluminum tube was therefore raised to 540° C. before a correct acetaldehyde–air mixture was supplied to it at 200 cc./min. Ignition failed to occur although in the earlier experiments, E.I.T. was 176° C. lower at 364° C. The rates of oxygen reacted and of carbon oxides formed when the combustion tube was maintained at 540° C. and rate of correct mixture supply varied from 50 to 200 cc./min. are given by Table IV. Comparable rates are given for correct pentane–air mixtures by Table V.

TABLE IV

CORRECT ACETALDEHYDE–AIR MIXTURES, OXYGEN REACTED AND CARBON OXIDES FORMED. ALUMINUM COMBUSTION TUBE AT 540° C. MAX. TEMPERATURE

Flow rate, cc./min.	$\%O_2$ reacted	$\%O_2$ reacted to form CO_2	$\%O_2$ reacted to form CO
50	51.6	20.0	12.2
100	45.0	14.0	11.6
150	44.0	12.3	11.2
200	43.1	11.2	11.0

TABLE V

CORRECT PENTANE–AIR MIXTURES, O_2 REACTED AND CARBON OXIDES FORMED. ALUMINUM COMBUSTION TUBE AT 540° C. MAX. TEMPERATURE

Flow rate, cc./min.	$\%O_2$ reacted	$\%O_2$ reacted to form CO_2	$\%O_2$ reacted to form CO
50	44.1	8.7	8.5
100	36.2	7.0	7.4
150	35.6	6.1	6.2
200	33.5	5.5	5.3

It will be seen by comparing the data of Tables IV and V that oxygen was reacted at the greater rate when acetaldehyde–air mixtures were supplied to the tube. The percentage reacted to form carbon oxides was approximately 100% greater than for the pentane–air mixtures. This may be taken to indicate that steam was formed at the greater rate when the acetaldehyde was oxidized.

C. STEEL COMBUSTION TUBE EXPERIMENTS

The temperatures of the explosive ignition of correct mixtures with air of acetaldehyde and pentane supplied to a stainless steel combustion tube at 200 cc./min. were given earlier, Table I, as 730 and 670° C. respectively.

Experiments made with other rates of mixture supply and values of mixture strength are described in this section. In addition to providing interesting data for the relative effects of a steel surface on the oxidation and ignition of acetaldehyde and pentane, the experiments indicate that two stage ignition of both substances might be possible in steel tubes in suitable conditions of flow configuration and temperature.

Effect of Rate of Supply, Correct Mixtures

The values of E.I.T. observed when the mixtures were supplied to a stainless steel tube at 100 to 475 cc./min. are tabulated below.

TABLE VI

EXPLOSIVE IGNITION IN A STAINLESS STEEL TUBE

Rate of mixture supply, cc./min.	E.I.T., ° C.	
	Pentane	Acetaldehyde
100	No ignition	No ignition
200	670	730
300	629	696
475	589	662

It will be noted that in the flow configuration conditions of the experiment, the values of E.I.T. for both substances diminished with decreasing time of exposure. Ignition did not occur with the relatively low rate of mixture supply of 100 cc./min. and as the rate was increased from 200 to 475 cc./min. values of E.I.T. diminished by 81 and 68° C. for pentane and acetaldehyde respectively.

Rates of Pre-explosion Oxidation

A series of experiments was carried out at rates of correct mixture supply ranging from 100 to 475 cc./min. Combustion tube temperatures were raised slowly by successive steps until explosion occurred or the limit of temperature measurement was reached. Tube temperature and rate of mixture supply were stabilized at every step while samples of the gases passing out of the tube were taken for analysis. The graphs of Fig. 7 for the relation between percentage of oxygen reacted and maximum tube temperatures with a rate of mixture supply of 200 cc./min. are typical of the series. The rates of oxygen reacted at E.I.T. for the several rates of mixture supply used for the experiments as given by the series of graphs are tabulated below.

The analysis results given in Table VII show that reaction of the oxygen in the mixtures when they were supplied at 100 cc./min. went substantially to completion without the occurrence of ignition. The reaction of the oxygen was little less than complete when the mixtures were supplied at 200 cc./min. and values of E.I.T. of the correct mixtures with air of acetaldehyde and pentane were 730 and 670° C. respectively. However on increasing rates of mixture

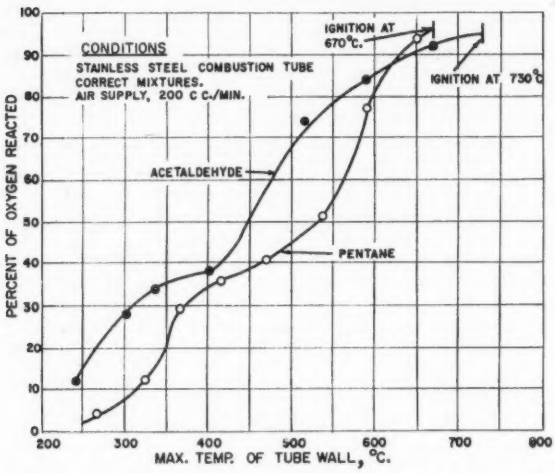

FIG. 7. The relation between percentage of oxygen reacted and the maximum temperature of a stainless steel combustion tube, correct mixtures with air of acetaldehyde and of pentane supplied at 200 cc./min.

TABLE VII

RATES OF OXYGEN REACTED AT TEMPERATURES OF THE EXPLOSIVE IGNITION OF CORRECT MIXTURES OF ACETALDEHYDE AND PENTANE WITH AIR

Rate of mixture supply, cc./min.	Acetaldehyde		Pentane	
	E.I.T., ° C.	% O_2 reacted	E.I.T., ° C.	% O_2 reacted
100	None	96	None	99
200	730	95	670	96
300	700	90	629	86
475	662	68	589	62

supply to 300 and 475 cc./min. significant decreases in rates of oxygen reacted, which corresponded with decreases in the temperatures of explosive ignition, were obtained. The experimental results show also that although the aldehyde was oxidized at a higher rate than the pentane, its ignition required a higher tube temperature.

The rates of oxidation, as given in Table VII, were determined from samples of the exit gases. They are therefore not the rates at the midsection of the tube where the temperature was a maximum and ignition occurred. More significant results for the relative rates of oxidation of acetaldehyde and pentane are given by analyses of samples taken at temperatures ranging upwards from those at which reaction occurs at an appreciable rate. Relative rates of reaction at temperatures rising from 250° C., as given by the graphs of Fig. 7, are given

in Table VIII. It is to be remembered in considering the results exhibited by the table that the correct mixtures of acetaldehyde and pentane contained 8.0 and 2.5 moles of oxygen, respectively, to 1 mole of the combustible substances.

TABLE VIII

PERCENTAGES OF AVAILABLE OXYGEN REACTED IN A STAINLESS STEEL COMBUSTION TUBE, TEMPERATURE RANGE 250 TO 600° C., CORRECT MIXTURES WITH AIR OF ACETALDEHYDE AND PENTANE

Max. temp. of tube, ° C.	% reacted of available oxygen	
	Acetaldehyde	Pentane
250	15	2
300	28	8
400	38	34
500	68	45
600	86	82

Effect of Mixture Strength on E.I.T.

The results of experiments made when using a mild steel tube, with a particular rate of mixture supply, namely 200 cc./min., and with mixture strength as a variable factor, are given by the graphs of Fig. 8. They show that for mixtures 25% rich, acetaldehyde and pentane possess the same degree of inflammability, values of E.I.T. being then nearly identical at 680° C.; but as mixture strength is reduced, the inflammability of the acetaldehyde diminishes with greater rapidity than that of pentane. Thus for mixtures 25% weak, a tube temperature of 800° C. was required for the ignition of the acetaldehyde and of 640° C. only for the pentane.

Temperatures of nonexplosive ignition, as indicated by pressure oscillations, are shown by the broken lines of the graphs of Fig. 8. Such ignition occurred in pentane–air mixtures leaner than 50% weak and more than 25% rich and in acetaldehyde–air mixtures solely for those more than 50% rich. Non-

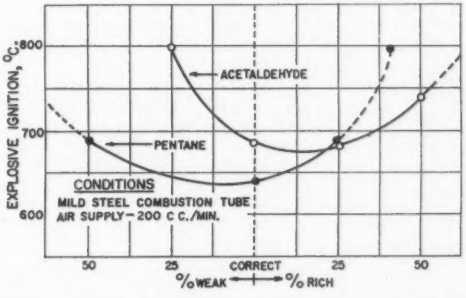

FIG. 8. Temperatures of explosive ignition of mixtures with air of acetaldehyde and of pentane as affected by mixture strength; mild steel tube, mixtures supplied at 200 cc./min.

explosive ignitions are, according to experiments described earlier, indicative of a low-temperature first-stage ignition. A possible explanation of the effect in a steel tube is that when the midsection of the combustion tube is at temperatures of 690° C. and over, as required for explosive ignition, temperature and flow configuration conditions suitable for a first stage ignition may exist in a lower and cooler section of the tube.

IV. DISCUSSION

The gaseous combustible mixture, when ignited in the conditions of the experiments of this Part, was diluted with oxidation products formed during its passage up the combustion tube to the position of maximum temperature. This position varies slightly with furnace temperature but may be described for convenience of reference as the midsection of the length of the tube within the furnace. The midsection temperature required for an igniting effect depends therefore on the degree of inflammability of the mixture at that position. This factor depends in turn on the extent of dilution of the mixture with oxidation products and *their* degree of inflammability.

The oxidation reactions that affect ignition temperature occur therefore below the midsection of the tube. The flow configuration in this length, as determined by experiment, was described in the introductory section. The flow was not unidirectional and laminar with the maximum velocity at the longitudinal axis, as would be expected according to Reynolds Numbers. It formed instead a closed convection circulation with a thin stream ascending along the heated wall and a descending central stream. A state of random turbulence existed between the oppositely moving streams. In these circumstances, the gaseous mixture entering the lower end of the tube necessarily joined the stream ascending along the wall to the position of maximum temperature. This thin stream may be regarded as a boundary layer having temperature gradients both vertically and horizontally. It must therefore be turbulent and as it surrounds the region of random turbulence, there must be a continuous interchange of gas between the oppositely moving streams. The impact of the random turbulence on the boundary layer is considered to be an important factor in respect of reaction velocity. Confirmatory experiments will be described in a subsequent paper.

When a combustion tube is set up concentrically in a vertical tubular furnace and the temperature is uniform at any cross section, the flow configuration in a gaseous mixture passing through it will be determined by the convection currents set up by temperature gradients along the wall and will be symmetrical about the longitudinal axis. The velocities of the convection circulation and the accompanying random turbulence will increase with increase in the temperature gradient. Thus it appeared to be possible, with the rates of mixture supply used for the experiments described in this Part, to heat the gaseous mixture entering the tube at room temperature to that of the midsection, although the heated length of tube below that section and within the furnace was $3\frac{1}{2}$ in. only.

The flow configuration as described would be expected to promote surface oxidation reactions and it is of interest to discuss their influence on the midsection temperature of the tube required for the ignition of a gaseous combustible mixture passing through it. This temperature is necessarily dependent on the degree of inflammability of the mixture in the boundary layer after its passage upward along the tube to the midsection. The reacting substance will then have been oxidized in part to final and partial products, and in similar conditions of flow configuration and rate of supply, the proportion of oxygen reacted and the respective concentrations of the possible oxidation products in the boundary layer will vary with the surface activity of the tube. The consequent phenomena of oxidation and ignition are especially well illustrated by the experiments of this Part with combustion tubes of steel and silica. Flow configuration in these tubes did not differ significantly according to the respective temperature gradients, which tended to become similar as the temperature was raised, and the thermal conductivity of the silica increased while that of the steel decreased.

Ignition in Steel Combustion Tubes

Pentane or acetaldehyde in correct mixtures with air, supplied to either mild or stainless steel tubes at 100 cc./min., was oxidized in the boundary layer so nearly to the final products, steam and carbon dioxide, that ignition was not possible. Ignition of correct mixtures in the stainless steel tube occurred on increasing the rate of mixture supply to 200 cc./min., at midsection temperatures of 670 and 730° C. for the pentane and acetaldehyde mixtures respectively; in the mild steel tube the respective ignition temperatures were lower at 644 and 685° C. respectively, Table I. The respective ignition temperatures in the stainless steel tube, for example, were reduced to 589 and 662° C. on increasing the rate of correct mixture supply to 475 cc./min., Table VI. If ignition had occurred in the gaseous phase as a result of slow combustion therein, the temperature required for the effect would have decreased with an increase in the time of exposure of the combustible mixture to the oxidizing conditions. The occurrence of the opposite effect is attributed to the decrease in the dilution of the boundary layer with final oxidation products and the consequent increase in inflammability as the rate of mixture supply was increased, remembering that the area of active surface remains constant irrespective of the rate of mixture supply. Similarly the acetaldehyde–air mixtures required a higher midsection temperature for ignition than the pentane–air mixtures on the steel surface because acetaldehyde was oxidized more rapidly than pentane, see Fig. 7. The experiments indicate that ignition in the steel tubes was an effect depending on the temperature of the midsection of the tube and the inflammability of the mixture in the boundary layer at that position.

Ignition in a Silica Combustion Tube and an Aldehyde Peroxide Hypothesis

Ignition in a silica tube, unlike the effect in steel tubes, occurred in high and low temperature ranges. This phenomenon is attributed fundamentally to

lower activity of the silica surface to oxidize the boundary layer to steam and carbon dioxide than that of the steel surface, and to the increase of the proportion of these final products in the boundary layer with increase of wall temperature. Fluorescence and cool flames were observed in the low-temperature range when mixtures with air of either pentane or acetaldehyde were supplied to the silica tube. A special furnace with a longitudinal slit in the wall was used for the observations. The phenomena have been described by many others and it is generally agreed that they precede ignition in the low-temperature range. In this range ignition in the silica tube appeared by visual observation to occur in the gaseous phase.

There is no general agreement in respect of the mechanism by which an oxidation reaction leads to ignition in the strictly gaseous phase other than that the formation of peroxides of the reacting substance is considered to be essential to a chain reaction mechanism. A comprehensive discussion of the mechanism of ignition in the low-temperature range would require a lengthy review of the work of many others and in any event is best deferred until further experiments on the effect of flow configuration are described. In the meantime a useful purpose will be served by outlining an hypothesis consistent with the results of experiments described in this Part, because it has provided a useful guide for further research. The hypothesis is based on the view that aldehyde peroxides, not alkyl or alkyl hydrogen peroxides as assumed by some (1, 8, 3), are those effective to initiate the reactions leading to ignition in the gaseous phase, and whether the aldehyde peroxides react further by a chain mechanism until ignition occurs as suggested by von Elbe and Lewis (14) or decompose to provide material nuclei of ignition need not be discussed at present.

In applying the hypothesis to the results of the flow configuration experiments of this Part, it may safely be assumed that oxidation started at the source of heat supply, namely the wall of the combustion tube, and that the products were carried from the boundary layer into the central stream by convection currents. The nature of these products is of special significance and has been determined by experiments to be described in a subsequent Part. According to these experiments, the initial products of the surface oxidation of pentane, as found in the boundary layer, tended to be aldehyde and water with traces of acids; there were no peroxides. It must be assumed therefore that peroxides found by analysis of the effluent from the combustion tube are formed by collisions of aldehyde molecules or corresponding acyl radicals carried from the boundary layer into the central stream with oxygen molecules therein.* The consequent oxidation and ignition characteristics of pentane and acetaldehyde, as determined by experiment, will now be discussed.

Pentane–Air Mixtures in Silica Tube, Oxidation and Ignition Characteristics

It will be seen by reference to Fig. 5 that reaction began when the maximum

* *It should be noted here that generally used methods for the determination of peroxide concentration in combustion products are based on measurements of the active oxygen; thus the nature of the peroxide is not determined.*

wall temperature of the tube was approximately 300° C. The reaction was accompanied by the passage of cool flames through the tube and the profuse formation of aldehyde, which is a well-known result of the oxidation of paraffins at relatively low temperatures, and is illustrated by the rapid rate of oxygen reacted in the temperature range 300 to 350° C., as shown by the graphs of the figure. The aldehyde formed on the surface and present in the boundary layer is, because of the flow configuration, carried into the central stream. The aldehyde peroxides then formed are, according to the hypothesis, responsible for the low-temperature ignition as indicated by the observed pressure waves. These mild and always nonexplosive ignitions were of maximum intensity at a midsection tube temperature of 325° C. for correct pentane–air mixtures supplied at 200 cc./min., and as shown by graph A of Fig. 3, this value remained nearly constant for mixtures ranging from 25% weak to 75% rich. The fluorescence and the pressure waves tended to die out as the temperature was raised. The concentration of final oxidation products in the boundary layer increased accordingly and pressure waves were not detectible at temperatures higher than 350° C. It will be seen, Fig. 5, that on continuing to raise the temperature, rate of oxygen reacted remained nearly constant until high-temperature ignitions were about to occur. These occurred at temperatures of 505, 510, and 570° C. for mixtures 25% rich, correct, and 25% weak, respectively; the temperatures are in fair agreement with those shown by graph B of Fig. 3, for experiments made earlier. The high-temperature ignitions are, as for the steel tube, believed to be a surface effect which depends on the inflammability of the boundary layer at the position of maximum temperature.

The nearly constant rate of oxygen reacted over the temperature range extending from 350° C. to 500° C., approximately, requires explanation. It is attributed to the negative temperature coefficient of reaction being concealed by surface oxidation reactions occurring over a range of temperature as the boundary layer ascends the temperature gradient of the tube wall. A negative temperature coefficient is usually obtained when the flow method is used and the reactor is uniformly heated as temperature is raised. In these conditions the phenomenon was first observed by Pease (9) and examples of it are exhibited by the graphs of Part II (5).

Acetaldehyde–Air Mixtures in Silica Tube, Oxidation and Ignition Characteristics

The acetaldehyde–air mixtures were supplied to the combustion tube at the rate used for the experiments with pentane, namely 200 cc./min.

The preliminary oxidation required for the formation of aldehyde peroxide from pentane was not required for the experiments with acetaldehyde. Reaction with oxygen started at temperatures approximately 100° C. lower than when pentane was used in similar conditions, compare Figs. 4 and 5. Fluorescence and cold flames appeared immediately, with ignitions occurring in the temperature range 225 to 275° C., depending on mixture strength, see Figs. 2 and 4. On continuing to raise the temperature, the intensity of the fluorescence diminished as did the magnitude of the pressure oscillations. These effects had disappeared when temperatures attained values of 350° C.

for mixtures 25% weak and 400° C. for mixtures 25% rich. High-temperature ignition of mixtures 25% weak, correct, and 25% rich occurred at 570, 510, and 505° C. respectively.

The results of experiments made to determine definite values for the high and low ignition temperatures for mixtures ranging from 50% weak to nearly 40% rich are shown by the graphs of Fig. 2. The low-temperature ignitions were not explosive for a mixture 50% weak but increased in intensity as mixture strength was increased to become definitely explosive for correct mixtures, and of increasing violence as mixture strength was further increased. This characteristic is due, according to the aldehyde peroxide hypothesis, to the increasing concentration of acetaldehyde in the mixture with air.

The high-temperature ignitions were always explosive. They occurred at temperatures ranging from 500° C. for mixtures 25% rich to 700° C. for those 75% weak. The relation between mixture strength and explosive ignition is similar to that observed for experiments with steel tubes. The experimental results indicate accordingly that high-temperature ignition in the silica tube is as with the steel tube a surface effect occurring at a temperature depending on the inflammability of the boundary layer.

The experiments with acetaldehyde show that ignition in the two temperature ranges does not arise from a common cause, the high-temperature ignition being a surface effect and the low-temperature ignition being an effect in the gaseous phase. They were for this reason obtainable independently as described in earlier text, Section IIIA, and as shown by the graphs of Fig. 2. This characteristic is not apparent when experiments are carried out in closed reactors. The results then obtained appear to show that high-temperature ignition occurs as a consequence of reactions beginning in the low-temperature range.

Ignition in Light Metal Tubes

Similar igniting effects were obtained in aluminum and magnesium tubes. The experimental results given in Section IIIB for aluminum tubes may therefore be regarded as typical. The ignition temperatures for acetaldehyde–air mixtures are little higher than those observed for the ignition of pentane–air mixtures in the low-temperature range, in a silica tube, for correct mixtures; for example, ignition of the acetaldehyde occurred at 350° C., Fig. 6, in the aluminum tube; pentane at 325° C. in the silica tube, Fig. 3. This and the fact that ignition did not occur when acetaldehyde–air mixtures were admitted to the tube after the temperature had been raised to 540° C. indicate that ignition would have been obtained in a higher temperature range if the tube could have been raised to the required degree without melting. The failure to obtain ignition of pentane–air mixtures in a low-temperature range is due, according to the aldehyde peroxide hypothesis, to surface oxidation not providing a sufficient concentration of aldehyde in the boundary layer. This assumption remains to be verified by experiment.

ACKNOWLEDGMENTS

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REFERENCES

1. CALLENDAR, H. L., KING, R. O., MARDLES, E. W. J., STERN, W. J., and FOWLER, N. R. Aeronaut. Research Comm. Repts. & Mem. No. 1062. 1926.
2. CALLENDAR, H. L., KING, R. O., and SIMS, C. J. Aeronaut. Research Comm. Repts. & Mem. No. 1013. 1925.
3. EGERTON, A., SMITH, F. L., and UBBELOHDE, A. R. Trans. Roy. Soc. (London), A, 234: 433–521. 1935.
4. JOST, W. Explosion and combustion processes in gases. *Translated by* Huber O. Croft. McGraw-Hill Book Company, Inc., New York and London. 1946.
5. KING, R. O. Can. J. Research, F, 26: 36–56. 1948.
6. KING, R. O. Can. J. Research, F, 26: 426–440. 1948.
7. KING, R. O. and DAVIDSON, R. R. Can. J. Research, A, 21: 65–67. 1943.
8. MOUREU, C., DUFRAISSE, C., and CHAUX, R. Compt. rend. 184: 413–417. 1927.
9. PEASE, R. N. J. Am. Chem. Soc. 51: 1839–1856. 1929.
10. PRETTRE, M. Compt. rend. 193: 240–242. 1931.
11. PRETTRE, M. L'inflammation et la combustion explosive en milieu gazeux. Part II. Hermann & Cie, Paris. 1934.
12. PRETTRE, M., DUMANOIS, P., and LAFFITTE, P. Compt. rend. 191: 329–31; 414–416. 1930.
13. RUMFORD, BENJAMIN, COUNT OF. Essays, political, economical and philosophical. Vol. II A. Strahan, Printers Street, London. 1800.
14. VON ELBE, G. and LEWIS, B. J. Am. Chem. Soc. 59: 976–984. 1937.

APPENDIX

Temperature Measurement

A wire ring comprising two chromel–alumel junctions in parallel and diametrically opposite was fitted tightly over the combustion tubes at the position of maximum temperature in the annulus between the furnace wall and the outside wall of the combustion tube. Temperatures were measured by using a precision potentiometer to balance the thermoelectric potential against that of a standard cell. Temperatures thus measured were found to be approximately 20° C. higher than those on the inside wall of either a steel or a vitreous tube. The upper limit of temperature measurement was 800° C.

Measurement of Rate of Air Supply

Air used for the experiments was from high-pressure cylinders and was therefore nearly dry. The air from a cylinder discharged through a two stage regulator with an adjustable outlet valve. Fine adjustment of the rate of air flow was attained by using a constant head device consisting of a tee tube having a vertical leg immersed in a water column open to the atmosphere. A nearly constant flow of air at any particular rate was obtained by adjustment of the height of the water column. The air from the constant head device was passed through a drying tower containing "Drierite", and then through a glass capillary tube to the combustion tube. Rates of air flow were determined by measuring the pressure difference across the capillary with a single-leg oil

manometer. Capillaries of required capacities were calibrated by the displacement of water method and by measurement of the rate of travel of a soap film through a calibrated tube.

Measurement of Rate of Liquid Supply

The combustible liquid was supplied by a Rideal microdoser (7). With this apparatus the pressure generated by the gas liberated in an electrolytic cell is transmitted through a liquid seal to a vessel containing the combustible liquid, which is discharged through a capillary into a carburetor where it vaporizes and mixes with the air supply to the combustion tube. Liquid is discharged into the carburetor at a rate governed by the rate of gas liberated in the electrolytic cell and in turn by the electric current passing through it. The liquid seal is in contact with the combustible liquid and should not dissolve it. The seal was of water when pentane was used for the experiments; it was of mercury when acetaldehyde was used.

It has been reported* since the microdoser was described (7) that according to a calibration made by others, the rate of gas liberated in the electrolytic cell does not remain constant for a particular value of the electric current passing through it. The usual method of calibration is to measure the rate at which a thread of mercury is moved through a capillary tube by the gas liberated by a measured current through the cell. The pressures involved are extremely small and on repeating calibrations it was found that results uniformly consistent with Faraday's Law were obtained only when both the mercury and the capillary were chemically clean. Chemical cleanliness is, of course, not of importance when the discharge capillary is filled with liquid which wets the glass. The pressures required to move liquid from the microdoser to the carburetor at small rates of flow, through a short and relatively large diameter capillary, are extremely small. Measurement will therefore not be accurate if pressures in the reactor are fluctuating, as for example when cold flames are passing through the combustible mixture in the reactor. On the other hand, the microdoser provides a useful visual indication of the presence of the cold flames which precede and follow ignition in the low-temperature range as temperature is raised.

Measurement of Rates of Pre-explosion Reactions

The gaseous mixtures issuing from combustion tubes were passed through three condenser traps. The first was cooled in ice-water. The second and third in dry ice – acetone mixtures. Gas samples were taken from the exit of the third trap through a T-tube bypass into an Orsat gas analysis apparatus for measurement of the rates of oxygen reacted and of the formation of carbon oxides. The samples were analyzed immediately after they were taken. At least 30 min. was required for each sample. There was thus sufficient time for the obtaining of steady conditions of temperature and pressure before another sample was taken at a higher temperature. The process of taking and analyzing samples continued until explosion occurred or combustion tube temperature exceeded that measurable by the thermocouples used.

* *Private communication.*

NOTE ON THE CORRELATION OF SOLUBILITY DATA

By A. I. Johnson, Chen-Jung Huang, and Ti-Kang Kwei

INTRODUCTION

The literature reports some equations (1, 2, 5), which have been derived experimentally and theoretically, relating solubility and temperature or expressing the temperature coefficient of solubility. These methods generally require data such as activity coefficients which may not be known or are not easily obtained for a particular system. The equation most extensively used for over 50 years may be written in the form of a linear expression of $\ln N$ and $1/T$, the ideality of the solution being assumed. Many such plots were given by Hildebrand (2); however, the slopes of the lines obtained by plotting $\ln N$ and $1/T$ vary to some extent with temperature such that the extrapolation beyond the limit of the data causes deviation especially at relatively low temperatures. Further, it has been discussed by Schröder (7), Roozeboom (6), and Hildebrand (2) that ideal solutions are rarely to be expected when two polar substances such as water and salt are involved. Recently, Othmer and Thakar (4) proposed the graphical method for relating solubility and temperature by plotting the solubility of one compound against the vapor pressure of a reference substance so that the deviations from ideality are largely removed. Mathematically, their correlation can be expressed, for the same temperature, as

$$\ln N_1 = (\Delta H_1/L) \ln P + C_1. \qquad [1]$$

In their plots, for some solutes, such as sucrose in water, the plot gives a slight curve because of very major deviations from Raoult's or Henry's laws. These irregular cases are probably due to high solubility, high molecular weight, and possible varying hydration of the solute molecules.

However, the irregularities found on Othmer's plots can be removed by this proposed method of plotting the solubilities of compounds against the solubility of a reference compound whose chemical structure is similar to the former.

THEORETICAL DERIVATION

Equation [1] proposed by Othmer and Thakar (4) can be rearranged for Compound 1 in differential form as

$$\frac{d \ln N_1}{\Delta H_1} = \frac{d \ln P}{L}. \qquad [2]$$

A similar expression can be obtained for Compound 2 in equilibrium with its saturated solution

$$\frac{d \ln N_2}{\Delta H_2} = \frac{d \ln P}{L}. \qquad [3]$$

At the same temperature, the right-hand sides of equations [2] and [3] must be the same provided that the same substance is used as a reference.

Therefore

$$[4] \qquad \frac{d \ln N_1}{\Delta H_1} = \frac{d \ln N_2}{\Delta H_2}$$

or

$$[5] \qquad \ln N_1 = \frac{\Delta H_1}{\Delta H_2} \ln N_2 + C_2.$$

Equation [5] indicates that on log–log paper the plot of the solubility of a compound in a saturated solution against the solubility of a reference substance in the same solvent both at the same temperature should result in a straight line provided the ratio of heat content ΔH_1 to ΔH_2 is constant with temperature.

USE OF THE CORRELATION

Figs. 1, 2, and 3 illustrate the proposed correlation using fatty acids as solutes and cyclohexane, benzene, and *n*-butanol as solvents. The application of the proposed method for inorganic salts is illustrated in Fig. 5. Fig. 4, the plots of solubilities of saccharides using maltose as a reference, shows that the irregularity found on Othmer's plot (4) can be eliminated in the proposed method. The data for these plots are from Markley (3) for solubilities of fatty acids in organic solvents, and from Seidell (8) for others.

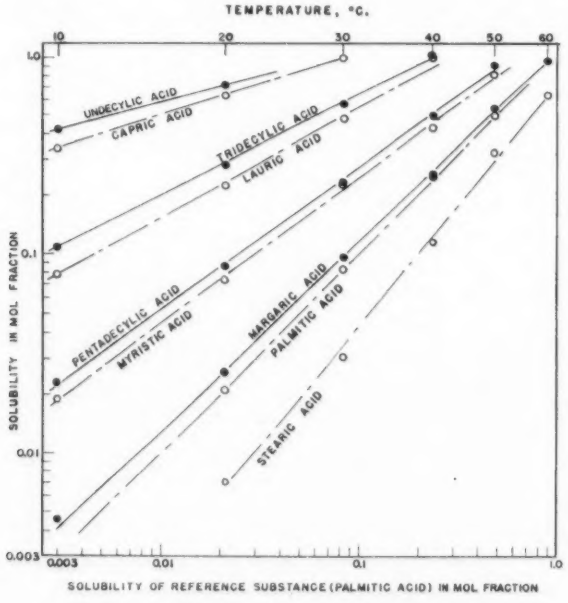

FIG. 1. Solubilities of fatty acids in cyclohexane.

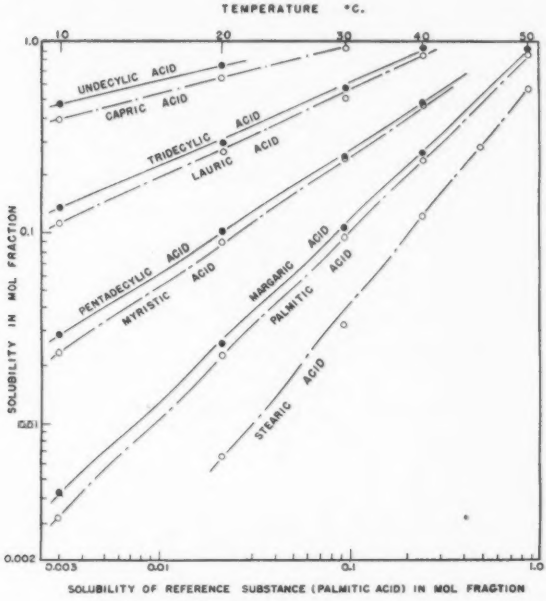

FIG. 2. Solubility of fatty acids in benzene.

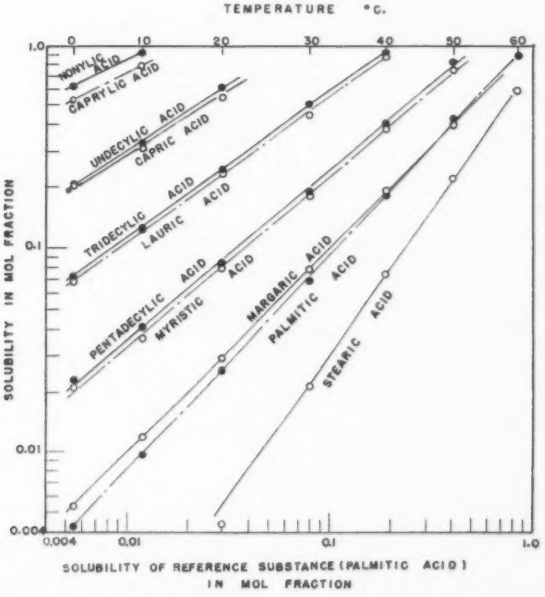

FIG. 3. Solubility of fatty acids in *n*-butanol.

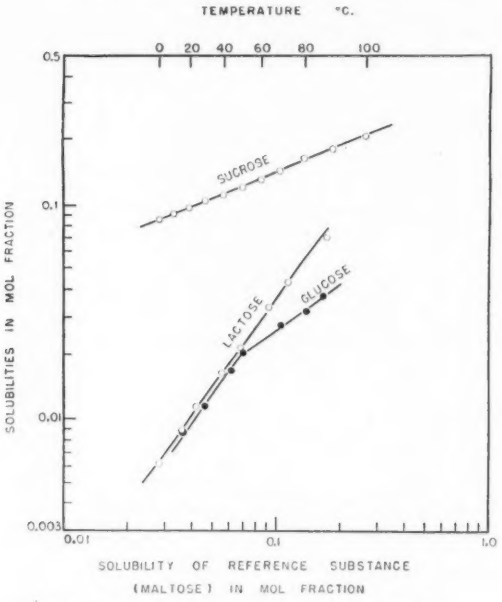

FIG. 4. Solubilities of saccharides in water.

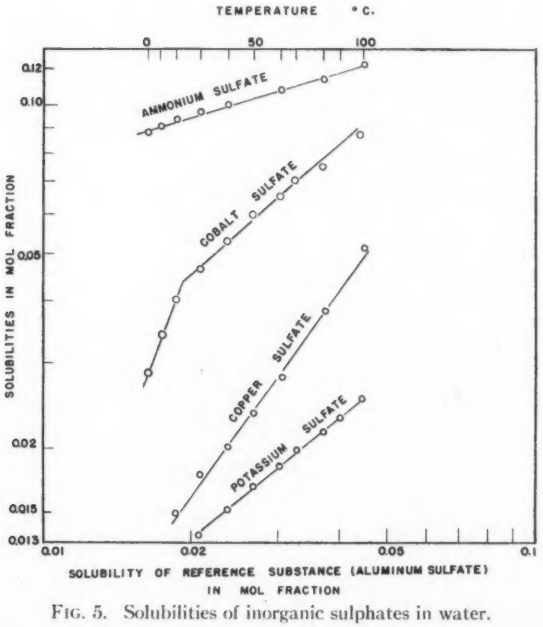

FIG. 5. Solubilities of inorganic sulphates in water.

The slope of the straight line on the proposed graphical correlation should be equal to the ratio of ΔH_1 to ΔH_2. But comparison with experimental values is made impossible as the thermal data for ΔH are very scarce. However, the straight lines obtained in the plot would reflect the soundness of the proposed correlation.

The data for several compounds, instead of giving continuous straight lines on log–log plots, give lines which are made up of straight sections with different slopes. It is very likely that these breaks correspond to some changes in the chemical forms of the solutes in the solution. The heat of transition from one form to the other causes a change in ΔH; thus an abrupt change in slope results at the temperature where the change in chemical form takes place. The break in the line for glucose in Fig. 4 indicates a change in solid phase from $\alpha C_6H_{12}O_6 \cdot H_2O$ to $\alpha C_6H_{12}O_6$ with decreased temperature coefficient. In the proposed method, the temperature scale can be superimposed based on the solubility of a reference substance.

It is noted on the plots of solubilities of fatty acids against the solubility of palmitic acid as reference in the same solvent that if the slopes of these lines are plotted against the number of carbon atoms, an alteration results as appeared in many other physical properties of fatty acids such as melting points and heat of crystallization. Fig. 6 supports this statement.

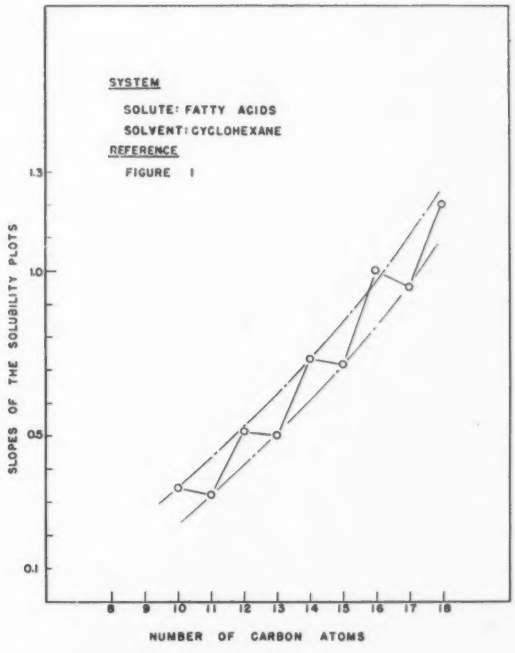

FIG. 6. Slopes of the solubility plots.

CONCLUSION

A method of correlating the solubility in the same solvent is proposed, plotting the solubility of a compound using a logarithmic scale against the temperature on an adjusted scale based on the solubility of a reference substance whose chemical structure is similar to the former.

The deviations from ideality and irregularity found on Othmer plots are eliminated in the proposed correlation. Therefore the correlation is believed to be useful for interpolating and extrapolating whenever two solubilities at different temperatures are known and when no further data are available.

NOMENCLATURE

T—Temperature, °K.

ΔH—Heat content. Difference between partial molal heat content of the solute in its saturated solution and the molal heat content of pure solid, or $(h_l - h_s)$ [heat of solution for 1 mole dissolving in (or negative of 1 mole crystallizing from) its saturated solution].

N—Solubility of solid in mole fraction.

P—Vapor pressure of a reference substance in Othmer plots.

L—Latent heat of vaporization of a reference substance in Othmer plots.

C_1—Constant.

C_2—Constant.

Subscripts:

l—Liquid.

s—Solid.

1—Substance 1.

2—Substance 2.

1. DAVIDSON, A. W. J. Chem. Educ. 10: 234. 1933.
2. HILDEBRAND, J. H. Solubility. 2nd ed. Reinhold Publishing Corporation, New York. 1936. pp. 13, 27.
3. MARKLEY, K. S. Fatty acids. Interscience Publishers, Inc., New York. 1947. pp. 191–197.
4. OTHMER, D. F. and THAKAR, M. S. Ind. Eng. Chem. 44: 1654. 1952.
5. OTHMER, D. F. and WHITE, R. E. Ind. Eng. Chem. 34: 952. 1942.
6. ROOZEBOOM, H. W. B. Die heterogenen Gleichgewichte. Vol. 2, Part 1. Friedrich Vieweg und Sohn, Braunschweig. 1904. pp. 267–287.
7. SCHRÖDER, I. W. Z. phys. Chem. 11: 499. 1893.
8. SEIDELL, A. Solubilities of inorganic and organic substances. D. Van Nostrand Co., New York. 1907. pp. 31, 122, 130, 262.
Supplement to second edition. 1928. p. 1290.
Third edition, Vol. II. 1941. pp. 711–717.

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Contents

Page

Iodophors as Sanitizing Agents—*C. K. Johns* - - - - - - - - - 71

Estimation of Protein Denaturation in Frozen Milk—*Dyson Rose* - 78

Effect of Freezing Rate on Stability of Frozen Milk—*Dyson Rose and H. Tessier* - 85

Thermodynamics of the Combustion of Sodium-base Pulping Liquors—*Thomas W. Bauer and Rodger M. Dorland* - - - - - 91

The Oxidation, Decomposition, Ignition, and Detonation of Fuel Vapors and Gases. XXIII. The Effect of Flow Configuration: *n*-Pentane and Acetaldehyde in Combustion Tubes of Various Materials—*R. O. King, S. Sandler, and R. Strom* - - - - - 102

Note on the Correlation of Solubility Data—*A. I. Johnson, Chen-Jung Huang, and Ti-Kang Kwei* - - - - - - - - - - - - 127

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